routine assays. For milks of exceptionally strong lipase activity it may be convenient to halve the sample size or the reaction period.

Initial pH

A series of buffers was prepared that gave a suitable range of pH when 0.6 ml. of tributyrin had been emulsified in 7 ml. of buffered milk. The pH values of the mixtures were determined at 30° C. at the start of the reaction period and lipase assays were made on a duplicate series. Fig. 4 shows the

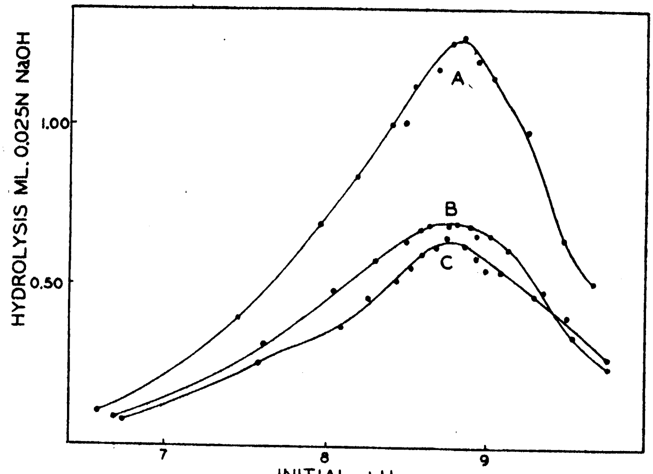

FIG. 4. *Initial pH and hydrolysis (three milks).*

curves obtained for three milks. While maximum hydrolysis occurred at approximately pH 8.75, this is not necessarily the optimum pH for milk lipase, because the hydrogen ion concentration does not remain constant throughout the reaction period. To study the buffer capacity of the borate buffer used in this procedure quadruplicate test tubes, each containing 7 ml. of buffered milk, were prepared. One tube was used for a pH determination at the beginning and one at the end of the reaction period. Lipase estimations were carried out on the remaining two tubes, one of them serving as a blank. The pH dropped as much as 0.40 unit in a highly lipolytic milk, as reported in Table I. It was found that no significant saponification occurred during the reaction period.

TABLE I

BUFFER CAPACITY OF SODIUM BORATE BUFFER

Milk	Initial pH 30° C.	Final pH 30° C.	pH difference	Hydrolysis
1	8.65	8.53	0.12	0.31
2	8.69	8.55	0.14	0.46
3	8.64	8.42	0.22	0.86
4	8.64	8.43	0.21	0.79
5	8.70	8.56	0.14	0.61
6	8.78	8.59	0.19	0.60
7	8.75	8.35	0.40	1.37
8	8.74	8.44	0.30	1.08

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THE PLOCHERE COLOR SYSTEM: A DESCRIPTIVE ANALYSIS[1]

BY W. E. KNOWLES MIDDLETON[2]

Abstract

The Plochere Color System is a collection of 1248 painted papers, the colors being produced by systematic pigment mixtures. The Munsell book notation of each of the samples is given, and certain regularities and singularities in the system are discussed.

Introduction

The Plochere Color System (8) is a collection of 1248 painted cards, each 3 by 5 in. in size, accompanied by an explanatory book, and intended mainly for the use of decorators. The system has had a brief notice (1) in the "News Letter" of the Inter-Society Color Council, but it is felt that a more detailed analysis will be of interest, partly as a matter of record, and partly to display some of the special features which may be expected in a system of colors arising from pigment mixtures.

For the Plochere System is quite frankly a pigment-mixture system. The accompanying book gives directions for the production of each of the 1248 colors by the mixture of one or more of only nine chromatic pigments with black and white, a feature of great interest to the decorator. The nine basic pigments and the special black are obtainable from the publishers of the system. The colors are classified into 26 blocks of 48 each, each set being intended to represent one hue, beginning with yellow and proceeding through orange, red, purple, blue, and green to a greenish yellow. It is stated that these hues represent the 24 hues of the Ostwald color circle (2) and two additional hues on either side of yellow, which were felt to give an improved gradation.

Each block of 48 colors is divided into six series of eight. Each of these series is intended to be at a certain chroma level, the first being the strongest in color and the sixth the least saturated. In each series the first color has the lowest value, the remaining seven being produced by extending this first color with increasing amounts of white.

The following Table I shows as an example the arrangement of the 48 colors classified as red, R, and numbered 337 to 384. Note that value as usually understood increases as we proceed downwards in this table. "The numbers

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[2] *Physicist.*

..... show the visual black content ..... The small letters give the white content of each color." (8, p. 3). The arrangement is stated to be based on the Ostwald triangle, but the "rectangular arrangement ..... seems to afford a more practical plan for displaying the entire scope of tones and shades of each hue." (8, p. 1).

TABLE I

"Chroma levels"

"Value levels"						
	R1a	R2a	R3a	R4a	R5a	R6a
	R1b	R2b	R3b	R4b	R5b	R6b
	R1c	R2c	R3c	R4c	R5c	R6c
	R1d	R2d	R3d	R4d	R5d	R6d
	R1e	R2e	R3e	R4e	R5e	R6e
	R1f	R2f	R3f	R4f	R5f	R6f
	R1g	R2g	R3g	R4g	R5g	R6g
	R1h	R2h	R3h	R4h	R5h	R6h

The system is certainly not intended as a set of standards, but is produced to meet certain practical needs. It is scarcely to be expected (especially in view of the very reasonable cost) that various examples will agree very closely among themselves, though we have no information on this point. For these reasons there was no thought of making spectrophotometric measurements on all the cards, even if personnel had been available to perform the immense labor of computing trichromatic co-ordinates. Such measurements were however made on one series (329 to 336) of very low chroma. The remainder of the cards were compared directly with the chips in the Munsell Book of Color, the trichromatic co-ordinates and reflectance of which are available (3, 5).

Comparison with the Munsell Book of Color

The cards were compared by one observer of normal color vision (the author), under MacBeth daylight, and in very uniform conditions, with the Pocket Edition of the Munsell Book of Color (6). Gray masks were employed. The copy of the Munsell book was purchased by the National Research Council in April 1947, and had been used very little up to the time of these comparisons.

The matching was made easier by the great similarity in the surface texture of the two sets of colors. On the other hand, many of the Plochere colors are much more saturated than any Munsell colors of similar hue, and many of the series go well above Munsell value 8/, the highest in the book. Thus a good deal of extrapolation was necessary, especially in chroma. Where the Plochere colors fell within the limits of the Munsell chips, it is felt that the accuracy of the matches was probably ± 0.5 for hue, ± 0.2 for value, and ± 0.4 for chroma. No attempt was made to smooth the run of the series, or to eliminate the small irregularities which became apparent; but a certain amount of unconscious smoothing was inevitable. One or two actual mistakes were discovered in plotting the results, and it is hoped that few others escaped

notice. Some of the very dark and unsaturated colors were difficult to assign a hue to, and the writer hesitates to estimate a probable error in hue where the value is less than 3/ and the chroma at the same time less than /1.

Results

The Munsell book notations, derived from direct matching (except for the series 329 to 336 inclusive, which is calculated from spectral reflectance curves), are shown in Table II. In this table the first column shows the Plochere reference number, the second the Plochere color notation, and the third the corresponding Munsell color. It was decided that the problem did not justify the conversion of the data to Munsell renotations, but this may be done for any desired color by the usual methods (7, p. 407).

The hue and chroma of the leading colors of each of the 156 series have been plotted in the polar diagram of Fig. 1. The numbered dots represent the leading colors of the 26 blocks. This clearly shows the reduction in chroma

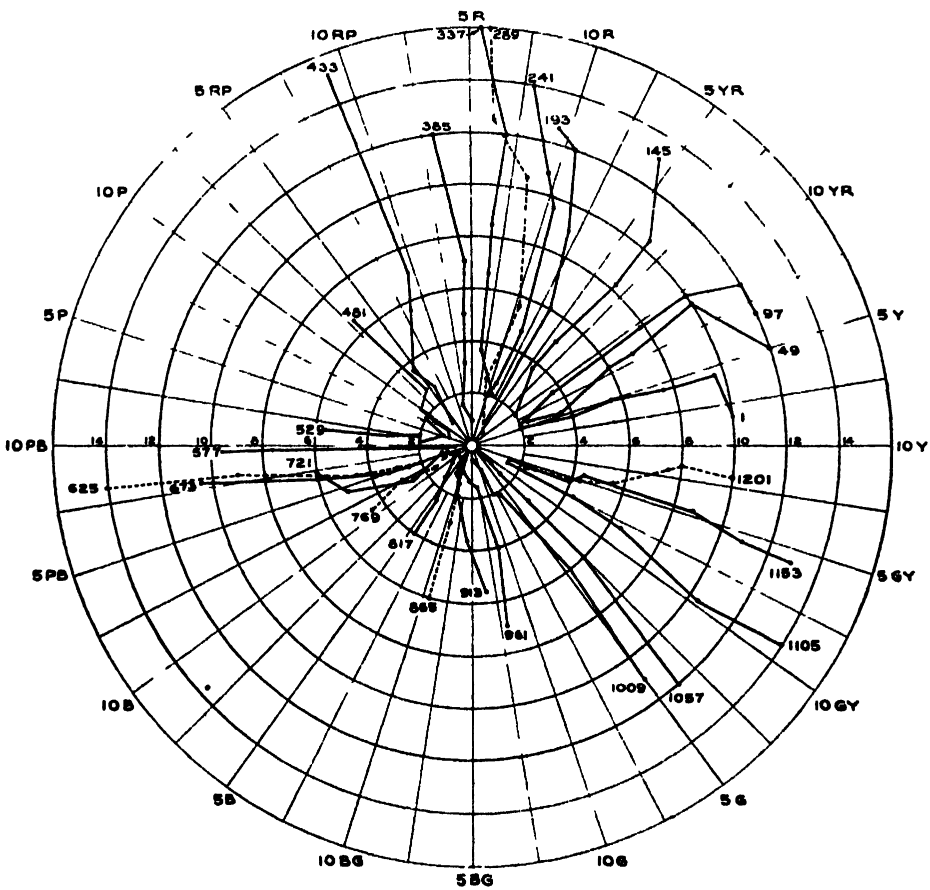

FIG. 1. *Polar diagram showing Munsell hue and chroma of the 156 leading colors in the 26 blocks. The numbers of the colors beginning the leading series of the blocks are given. The occasional use of dashed lines is only for clarity.*

TABLE II

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR

Plochere number	Plochere code	Munsell color		Plochere number	Plochere code	Munsell color	
1	Y 1–a	8.5Y	9/10	49	Yo 1–a	5Y	9/12
2	Y 1–b	8.5Y	8.5/9	50	Yo 1–b	6Y	9/11
3	Y 1–c	8Y	8.5/8	51	Yo 1–c	6.5Y	9/10
4	Y 1–d	9Y	8.5/7.5	52	Yo 1–d	7.5Y	9/8
5	Y 1–e	9Y	9/6	53	Yo 1–e	7.5Y	9/7
6	Y 1–f	9Y	9/4.5	54	Yo 1–f	7.5Y	9/6
7	Y 1–g	9Y	9/2.5	55	Yo 1–g	8.5Y	9/4
8	Y 1–h	8.5Y	9/1	56	Yo 1–h	?	>9/1
9	Y 2–a	5.5Y	8.5/9.5	57	Yo 2–a	1.0Y	7.0/10.0
10	Y 2–b	6.5Y	8.5/8.5	58	Yo 2–b	2.0Y	8.2/10
11	Y 2–c	7Y	9/7.5	59	Yo 2–c	4.0Y	8.4/9
12	Y 2–d	8Y	9/7	60	Yo 2–d	4.5Y	8.5/8
13	Y 2–e	8Y	8.5/6	61	Yo 2–e	5.5Y	9/6
14	Y 2–f	9Y	8.5/5.5	62	Yo 2–f	5.5Y	9/5
15	Y 2–g	10Y	8.5/3.5	63	Yo 2–g	6Y	9/4
16	Y 2–h	10Y	9/1	64	Yo 2–h	?	>9/2
17	Y 3–a	5.5Y	6.5/7.5	65	Yo 3–a	2.0Y	5.8/7.0
18	Y 3–b	5.5Y	6.8/7	66	Yo 3–b	2.5Y	5.8/7.5
19	Y 3–c	5.5Y	8/7.5	67	Yo 3–c	3.0Y	7.5/8.0
20	Y 3–d	7Y	8/6.5	68	Yo 3–d	3.5Y	8.3/6.7
21	Y 3–e	7.5Y	8.5/5	69	Yo 3–e	4.0Y	8.5/6.2
22	Y 3–f	8Y	8.5/4	70	Yo 3–f	4.5Y	9/5
23	Y 3–g	8Y	9/2	71	Yo 3–g	5Y	9/4
24	Y 3–h	9Y	9/0.5	72	Yo 3–h	5Y	>9/2
25	Y 4–a	5Y	5.8/5.5	73	Yo 4–a	2.0Y	5.6/6.0
26	Y 4–b	5Y	6.5/5.5	74	Yo 4–b	2.5Y	6.2/6.4
27	Y 4–c	5.5Y	7.2/5.5	75	Yo 4–c	3.0Y	7.2/6.2
28	Y 4–d	6Y	8/5.5	76	Yo 4–d	4.0Y	7.8/6.3
29	Y 4–e	7Y	8.5/5.5	77	Yo 4–e	4.0Y	8.3/5.6
30	Y 4–f	7Y	9/5	78	Yo 4–f	4Y	9/5
31	Y 4–g	7.5Y	9/5	79	Yo 4–g	3.5Y	9/3
32	Y 4–h	?	>9/?	80	Yo 4–h	?	>9/1
33	Y 5–a	5.5Y	4.2/4.0	81	Yo 5–a	4.5Y	3.7/3.6
34	Y 5–b	5.5Y	5.0/4.5	82	Yo 5–b	4.5Y	5.2/3.6
35	Y 5–c	5.5Y	6.2/4.0	83	Yo 5–c	4.0Y	5.8/3.6
36	Y 5–d	5.5Y	7.2/3.8	84	Yo 5–d	4.0Y	7.2/3.2
37	Y 5–e	5.0Y	8.0/3.8	85	Yo 5–e	3.8Y	7.8/3.2
38	Y 5–f	5.5Y	8.5/2.5	86	Yo 5–f	3.5Y	8.2/2.4
39	Y 5–g	6Y	9/2	87	Yo 5–g	3Y	9/2
40	Y 5–h	?	>9/?	88	Yo 5–h	?	>9/1
41	Y 6–a	4.5Y	3.5/2	89	Yo 6–a	3.5Y	3.8/2.2
42	Y 6–b	3.5Y	4.2/2	90	Yo 6–b	3.2Y	4.2/2.5
43	Y 6–c	3.0Y	5.7/2	91	Yo 6–c	4.0Y	5.3/2.5
44	Y 6–d	3.0Y	6.2/2.5	92	Yo 6–d	4.2Y	6.0/2.5
45	Y 6–e	3.0Y	7.2/2.5	93	Yo 6–e	5Y	7.2/2.7
46	Y 6–f	4.0Y	8.2/2	94	Yo 6–f	5Y	8.3/1.5
47	Y 6–g	5Y	8.8/2	95	Yo 6–g	5Y	9/1
48	Y 6–h	?	>9/?	96	Yo 6–h	?	>9/1

TABLE II—*Continued*

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR—*Continued*

Plochere number	Plochere code	Munsell color	Plochere number	Plochere code	Munsell color
97	OY 1–a	3.0Y 8/12	145	O 1–a	4.0YR 6.5/13
98	OY 1–b	2.5Y 8.2/11	146	O 1–b	7.5YR 7.7/12
99	OY 1–c	3.0Y 8.5/9.5	147	O 1–c	9.0YR 8.2/11
100	OY 1–d	3.5Y 9/9	148	O 1–d	2.0Y 8.7/8.5
101	OY 1–e	4.0Y 9/7	149	O 1–e	3.0Y 9.0/6.6
102	OY 1–f	4.5Y 9/4	150	O 1–f	3.5Y 9/5.3
103	OY 1–g	6Y 9/2	151	O 1–g	4Y 9/4
104	OY 1–h	?7.5Y >9/<1	152	O 1–h	? >9/?
105	OY 2–a	1.5Y 7.6/12	153	O 2–a	6.5YR 6.2/10.5
106	OY 2–b	2.5Y 8.0/12	154	O 2–b	8.0YR 7.0/9.8
107	OY 2–c	2.5Y 8.3/11	155	O 2–c	9.2YR 7.8/9.0
108	OY 2–d	3.2Y 8.5/8	156	O 2–d	1.0Y 8.2/7.6
109	OY 2–e	4Y 8.8/7	157	O 2–e	2.0Y 8.5/6.6
110	OY 2–f	4Y 9/5	158	O 2–f	2.5Y 9/6
111	OY 2–g	5Y >9/4	159	O 2–g	3Y >9/4
112	OY 2–h	? >9/2	160	O 2–h	? >9/3
113	OY 3–a	0.3Y 6.1/9 8	161	O 3–a	6.5YR 5.0/8.2
114	OY 3–b	0.6Y 7.1/9.8	162	O 3–b	6.8YR 5.8/8.4
115	OY 3–c	1.0Y 7.8/9.5	163	O 3–c	7.2YR 6.8/7.8
116	OY 3–d	2.5Y 8.2/8.5	164	O 3–d	8.7YR 7.2/6.5
117	OY 3–e	2.5Y 8.7/7.5	165	O 3–e	9.8YR 7.9/6.4
118	OY 3–f	2.5Y 8.8/6	166	O 3–f	1.2Y 8.4/4.7
119	OY 3–g	3Y 9/4	167	O 3–g	0.5Y 9/3.6
120	OY 3–h	? >9/3	168	O 3–h	? >9/2.5
121	OY 4–a	0.3Y 4.9/7.8	169	O 4–a	6.0YR 4.1/5.0
122	OY 4–b	0.3Y 5.8/7.5	170	O 4–b	7.0YR 5.3/5.6
123	OY 4–c	10.0YR 6.7/8.0	171	O 4–c	6.8YR 5.9/5.8
124	OY 4–d	0.5Y 7.3/6.0	172	O 4–d	8.0YR 7.0/5.8
125	OY 4–e	2.0Y 8.0/5.5	173	O 4–e	8.8YR 8.2/5.6
126	OY 4–f	2.5Y 8.3/5.3	174	O 4–f	9.3YR 8.5/4.5
127	OY 4–g	3Y 8.8/4	175	O 4–g	9.5YR 9/3.6
128	OY 4–h	3Y >9/3	176	O 4–h	?10YR >9/3
129	OY 5–a	1.0Y 3.6/3.6	177	O 5–a	6.0YR 3.3/3.6
130	OY 5–b	10.0YR 5.2/4.0	178	O 5–b	6.2YR 4.8/4.5
131	OY 5–c	0.5Y 5.7/3.6	179	O 5–c	7.5YR 5.3/4.5
132	OY 5–d	1.0Y 6.5/4.2	180	O 5–d	8.0YR 6.6/4.4
133	OY 5–e	1.2Y 7.5/4.4	181	O 5–e	8.3YR 7.2/3.6
134	OY 5–f	1.0Y 8 0/3.6	182	O 5–f	8.3YR 8.0/3.6
135	OY 5–g	1.0Y 8.8/3.6	183	O 5–g	8.0YR 8.7/3.5
136	OY 5–h	1.0Y 9/3	184	O 5–h	?8YR 9/3?
137	OY 6–a	4.5Y 3.3/2.0	185	O 6–a	1.0Y 2.3/2
138	OY 6–b	3.0Y 4.2/2.0	186	O 6–b	1.7Y 3.8/1.8
139	OY 6–c	3.5Y 5.2/2.6	187	O 6–c	8.5YR 4.9/1.8
140	OY 6–d	2.2Y 5.9/2.0	188	O 6–d	8.3YR 5.7/1 6
141	OY 6–e	3.2Y 7.2/2.0	189	O 6–e	8.0YR 6.7/2.0
142	OY 6–f	3.0Y 8.1/2.0	190	O 6–f	6.0YR 7.9/1.6
143	OY 6–g	3Y 8.8/2.0	191	O 6–g	5.0YR 8.8/1.5
144	OY 6–h	3Y 9/2	192	O 6–h	5YR 9/2

TABLE II—*Continued*

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR—*Continued*

Plochere number	Plochere code	Munsell color	Plochere number	Plochere code	Munsell color
193	Or 1–a	9.5R 6.0/12.5	241	RO 1–a	8.0R 4.8/14
194	Or 1–b	2.0YR 6.3/11.5	242	RO 1–b	9.5R 5.7/12
195	Or 1–c	3.2YR 6.9/9.6	243	RO 1–c	9.6R 6.2/10.4
196	Or 1–d	4.0YR 8.5/8	244	RO 1–d	1.5YR 6.8/8.5
197	Or 1–e	8.5YR 9/7	245	RO 1–e	2.5YR 7.8/6.0
198	Or 1–f	9YR 9/6	246	RO 1–f	4.5YR 8.5/4.8
199	Or 1–g	0.5Y >9/4	247	RO 1–g	5YR 9/4
200	Or 1–h	9YR >9/2	248	RO 1–h	?5YR >9/2?
201	Or 2–a	0.5YR 5.0/12	249	RO 2–a	9.5R 4.3/10.8
202	Or 2–b	2.0YR 5.8/11	250	RO 2–b	9.7R 5.3/10.3
203	Or 2–c	3.0YR 6.9/9.6	251	RO 2–c	9.7R 6.2/9.8
204	Or 2–d	5.0YR 7.5/8	252	RO 2–d	1.2YR 7.0/8.4
205	Or 2–e	6.5YR 7.8/7	253	RO 2–e	2.8YR 7.5/6.6
206	Or 2–f	8.5YR 8.3/5.5	254	RO 2–f	4.0YR 8.3/5
207	Or 2–g	1Y 9/4	255	RO 2–g	3YR 9/4
208	Or 2–h	?10YR >9/2	256	RO 2–h	? >9/?
209	Or 3–a	2.0YR 4.0/9.0	257	RO 3–a	0.5YR 4.0/9.5
210	Or 3–b	3.5YR 5.2/8.4	258	RO 3–b	1.0YR 4.6/8.0
211	Or 3–c	4.0YR 6.2/7.0	259	RO 3–c	0.8YR 5.4/7.5
212	Or 3–d	5.5YR 6.9/7	260	RO 3–d	1.0YR 6.5/7.2
213	Or 3–e	7YR 7.8/7	261	RO 3–e	2.2YR 6.9/6.0
214	Or 3–f	7.5YR 8/6	262	RO 3–f	3.0YR 8.2/4
215	Or 3–g	9YR 9/5	263	RO 3–g	3YR 8.8/4
216	Or 3–h	?8YR >9/4	264	RO 3–h	?3YR >9/?
217	Or 4–a	3.5YR 3.2/6.0	265	RO 4–a	1.8YR 3.3/4.7
218	Or 4–b	4.5YR 4.8/6.0	266	RO 4–b	2.5YR 4.0/4.8
219	Or 4–c	5.0YR 6.0/5.6	267	RO 4–c	2.2YR 5.1/4.0
220	Or 4–d	5.5YR 6.8/5.4	268	RO 4–d	3.0YR 6.0/4.5
221	Or 4–e	6YR 7.8/5	269	RO 4–e	4.0YR 6.8/4.5
222	Or 4–f	7YR 8/4 5	270	RO 4–f	3.0YR 7.7/4.0
223	Or 4–g	8YR 8.5/4	271	RO 4–g	3YR 8.7/3
224	Or 4–h	8YR 9/3	272	RO 4–h	?3YR >9/2?
225	Or 5–a	3.3YR 2.7/4	273	RO 5–a	1.0YR 2.8/2.4
226	Or 5–b	3.5YR 4.4/3.6	274	RO 5–b	0.5YR 3.7/2.6
227	Or 5–c	4.2YR 5.2/3.4	275	RO 5–c	10.0R 4.8/2.4
228	Or 5–d	4.6YR 5.9/3.5	276	RO 5–d	0.8YR 5.8/2.6
229	Of 5–e	4.5YR 7.0/3.2	277	RO 5–e	1.0YR 6.6/2.4
230	Or 5–f	4.5YR 7.8/3	278	RO 5–f	1YR 7.3/2
231	Or 5–g	5YR 8.7/3	279	RO 5–g	1YR 8.1/2
232	Or 5–h	6YR 9/3	280	RO 5–h	?1YR 9/2
233	Or 6–a	?4YR 2.2/2	281	RO 6–a	1.8YR 2.2/2
234	Or 6–b	?4YR 3/1	282	RO 6–b	4.0YR 3.5/2.0
235	Or 6–c	5YR 5/1	283	RO 6–c	4.4YR 4.9/2.0
236	Or 6–d	6YR 5.8/1	284	RO 6–d	4.0YR 5.7/2.2
237	Or 6–e	?3YR 6.5/1	285	RO 6–e	3.8YR 6.3/2.0
238	Or 6–f	5YR 7.8/1	286	RO 6–f	3.3YR 6.9/2
239	Or 6–g	5YR 8.5/1.5	287	RO 6–g	3.5YR 8.2/2
240	Or 6–h	?4YR >9/1?	288	RO 6–h	3YR 9/2

TABLE II—*Continued*

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR—*Continued*

Plochere number	Plochere code	Munsell color		Plochere number	Plochere code	Munsell color	
289	Ro 1–a	5.8R	4.6/16	337	R 1–a	6.0R	4.2/16
290	Ro 1–b	6.0R	5.3/13.0	338	R 1–b	4.5R	4.9/13
291	Ro 1–c	5.3R	5.6/10.8	339	R 1–c	3.5R	5.2/10.8
292	Ro 1–d	5.5R	6.3/10.0	340	R 1–d	2.5R	5.9/10.5
293	Ro 1–e	6.2R	7.3/9	341	R 1–e	1.5R	6.6/10
294	Ro 1–f	6R	7.7/7.5	342	R 1–f	1.0R	7.3/10
295	Ro 1–g	6R	8.5/6	343	R 1–g	1R	8/10?
296	Ro 1–h	6R	9/3?	344	R 1–h	?10RP	9/9?
297	Ro 2–a	6.8R	4.4/12.5	345	R 2–a	7.0R	3.8/12
298	Ro 2–b	6.3R	5.0/11.3	346	R 2–b	5.4R	4.4/10.5
299	Ro 2–c	5.8R	5.4/10.5	347	R 2–c	4.2R	5.2/9.5
300	Ro 2–d	5.8R	6.2/9.3	348	R 2–d	3.2R	6.0/10.0
301	Ro 2–e	5.8R	7.3/8.5	349	R 2–e	3.8R	6.7/9.2
302	Ro 2–f	6.3R	8.2/7	350	R 2–f	3.0R	7.5/8
303	Ro 2–g	6.5R	8.8/6	351	R 2–g	2R	8/7
304	Ro 2–h	6.5R	>9/5?	352	R 2–h	2R	9/6?
305	Ro 3–a	8.5R	3.5/10.5	353	R 3–a	6.8R	3.3/8.5
306	Ro 3–b	9.0R	4.3/9.0	354	R 3–b	6.0R	4.2/7.3
307	Ro 3–c	8.0R	5.2/7.6	355	R 3–c	6.0R	5.1/6.6
308	Ro 3–d	7.8R	6.2/7.6	356	R 3–d	4.5R	5.8/8.0
309	Ro 3–e	7.5R	7.0/6.6	357	R 3–e	4.5R	6.8/8.0
310	Ro 3–f	7.8R	7.7/7.0	358	R 3–f	4.0R	7.7/7.5
311	Ro 3–g	7.2R	8.2/5	359	R 3–g	4R	8.5/6
312	Ro 3–h	7R	8.7/4	360	R 3–h	3R	9/4
313	Ro 4–a	0.3YR	3.0/5.6	361	R 4–a	7.0R	3.2/6.6
314	Ro 4–b	1.0YR	3.7/5.5	362	R 4–b	6.2R	4.0/6.0
315	Ro 4–c	9.5R	5.0/4.7	363	R 4–c	5.5R	4.9/5.3
316	Ro 4–d	9.5R	5.8/4.4	364	R 4–d	4.5R	5.8/6.0
317	Ro 4–e	10.0R	6.8/4.4	365	R 4–e	4.5R	6.4/6.6
318	Ro 4–f	9.5R	7.6/4	366	R 4–f	3.0R	7.5/5.5
319	Ro 4–g	9R	8.5/3	367	R 4–g	3R	8.2/4
320	Ro 4–h	9R	9/3?	368	R 4–h	3R	9/3
321	Ro 5–a	9.0R	2.2/2.6	369	R 5–a	7R	2.4/3.6
322	Ro 5–b	9.0R	3.7/2.6	370	R 5–b	6.8R	3.6/3.6
323	Ro 5–c	8.8R	4.9/2.6	371	R 5–c	5.5R	4.9/4.0
324	Ro 5–d	8.3R	5.8/2.4	372	R 5–d	4.0R	5.7/4.8
325	Ro 5–e	7.5R	6.8/2.4	373	R 5–e	3.5R	6.7/5.3
326	Ro 5–f	7.5R	7.7/2.5	374	R 5–f	4.0R	7.6/5
327	Ro 5–g	7.5R	8.7/2	375	R 5–g	4R	8.2/4
328	Ro 5–h	?7.5R	9/2	376	R 5–h	4R	9/4
329	Ro 6–a	?7YR	2.4/0.5	377	R 6–a	1YR	2.3/2
330	Ro 6–b	5YR	3.6/0.6	378	R 6–b	8R	3.2/1.5
331	Ro 6–c	8YR	4.7/0.8	379	R 6–c	7.5R	4.8/1.5
332	Ro 6–d	10YR	5.3/1.0	380	R 6–d	6.8R	5.8/1.5
333	Ro 6–e	5Y	6.7/1.2	381	R 6–e	7R	6.5/2
334	Ro 6–f	10YR	7.6/0.7	382	R 6–f	6R	7.5/2
335	Ro 6–g	7YR	8.2/0.6	383	R 6–g	6R	8.2/2
336	Ro 6–h	5YR	8.6/0.6	384	R 6–h	6R	9/2

TABLE II—*Continued*

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR—*Continued*

Plochere number	Plochere code	Munsell color		Plochere number	Plochere code	Munsell color	
385	Rp 1–a	3R	3.2/12	433	Pr 1–a	9.0RP	3.2/15?
386	Rp 1–b	1.0R	4.2/12	434	Pr 1–b	7.5RP	3.9/13?
387	Rp 1–c	8.5RP	4.8/12	435	Pr 1–c	5.8RP	4.7/13
388	Rp 1–d	8.0RP	5.5/11.5	436	Pr 1–d	3.5RP	5.2/12
389	Rp 1–e	8.0RP	6.5/11	437	Pr 1–e	2.5RP	6.2/12
390	Rp 1–f	7RP	7.5/11	438	Pr 1–f	?3RP	7/12?
391	Rp 1–g	7RP	8.6/10?	439	Pr 1–g	?4RP	8/10?
392	Rp 1–h	7.5RP	9/8?	440	Pr 1–h	?5RP	9/8?
393	Rp 2–a	4.6R	3.1/7.0	441	Pr 2–a	9.5RP	3.0/7.0
394	Rp 2–b	1.5R	4.1/6.8	442	Pr 2–b	4.5RP	3.8/10.0
395	Rp 2–c	9.0RP	4.8/7.5	443	Pr 2–c	3.3RP	4.3/12
396	Rp 2–d	8.2RP	5.7/9.0	444	Pr 2–d	2.5RP	5.4/12
397	Rp 2–e	7.5RP	6.4/9.5	445	Pr 2–e	?3RP	6.3/12?
398	Rp 2–f	8RP	7/9	446	Pr 2–f	3RP	6.7/11
399	Rp 2–g	8RP	8/8	447	Pr 2–g	3RP	8/10
400	Rp 2–h	9RP	9/7	448	Pr 2–h	?3RP	9/8?
401	Rp 3–a	4R	2.8/5.0	449	Pr 3–a	8.5RP	2.3/5.6
402	Rp 3–b	0.5R	3.9/5.3	450	Pr 3–b	4.3RP	3.7/6.6
403	Rp 3–c	8.8RP	4.8/6.0	451	Pr 3–c	3.0RP	4.5/7.5
404	Rp 3–d	8.0RP	5.6/7.5	452	Pr 3–d	2.5RP	5.2/8.0
405	Rp 3–e	7.5RP	6.2/8.5	453	Pr 3–e	2.5RP	6.0/9
406	Rp 3–f	8RP	7.2/8	454	Pr 3–f	?4RP	6.8/9
407	Rp 3–g	9RP	8/8	455	Pr 3–g	4RP	7.8/8
408	Rp 3–h	9RP	9/7?	456	Pr 3–h	5RP	9/8
409	Rp 4–a	4R	2.2/3.3	457	Pr 4–a	4.0RP	2.3/3.5
410	Rp 4–b	1.0R	4.0/4.6	458	Pr 4–b	4.5RP	3.5/4.5
411	Rp 4–c	0.5R	5.0/4.4	459	Pr 4–c	3.5RP	4.6/5.5
412	Rp 4–d	8.3RP	5.7/5.6	460	Pr 4–d	3.0RP	5.1/6.0
413	Rp 4–e	9.0RP	6.4/5.3	461	Pr 4–e	3.5RP	5.8/5.6
414	Rp 4–f	9.0RP	7.1/6	462	Pr 4–f	3.2RP	7.0/6
415	Rp 4–g	9.6RP	8/5	463	Pr 4–g	3RP	7.8/6
416	Rp 4–h	10RP	9/5	464	Pr 4–h	4RP	9/5?
417	Rp 5–a	2.0R	1.8/1.5	465	Pr 5–a	6RP	2.8/2.7
418	Rp 5–b	8.5RP	3.5/2.5	466	Pr 5–b	3.5RP	3.9/3.3
419	Rp 5–c	8.0RP	4.3/3.3	467	Pr 5–c	3.5RP	5.0/4.0
420	Rp 5–d	8.0RP	5.3/4.0	468	Pr 5–d	3.0RP	5.8/4.5
421	Rp 5–e	9.2RP	6.3/4.5	469	Pr 5–e	4.0RP	6.4/4.5
422	Rp 5–f	8.8RP	7.1/4.7	470	Pr 5–f	3.5RP	7.2/4
423	Rp 5–g	9RP	7.8/5	471	Pr 5–g	3.0RP	7.9/4
424	Rp 5–h	10RP	9/5	472	Pr 5–h	3RP	8.5/4
425	Rp 6–a	6R	1.5/0.7	473	Pr 6–a	4.5RP	2.5/1.0?
426	Rp 6–b	2R	3.8/0.5	474	Pr 6–b	?1.0RP	3.3/1.0
427	Rp 6–c	6RP	4.3/1.0	475	Pr 6–c	1.8RP	4.5/2.0
428	Rp 6–d	3.5RP	5.3/1.3	476	Pr 6–d	0.5RP	5.3/2.5
429	Rp 6–e	3.5RP	6.5/1.3	477	Pr 6–e	10.0P	6.5/3.0
430	Rp 6–f	2.5RP	7.1/1.5	478	Pr 6–f	1.0RP	7.1/3.0
431	Rp 6–g	3.5RP	7.8/1	479	Pr 6–g	2.0RP	7.8/3.5
432	Rp 6–h	5RP	9/1	480	Pr 6–h	2RP	9/3

TABLE II—*Continued*

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR—*Continued*

Plochere number	Plochere code	Munsell color		Plochere number	Plochere code	Munsell color	
481	P 1-a	3.0RP	2.5/6.6	529	Pb 1-a	1.5P	2.5/5.6
482	P 1-b	2.5RP	3.8/9.4	530	Pb 1-b	3.8P	3.9/7.0
483	P 1-c	0.5RP	4.6/10.0	531	Pb 1-c	5.0P	4.8/8.5
484	P 1-d	1.0RP	5.6/9.6	532	Pb 1-d	5.0P	5.8/8.5
485	P 1-e	1.2RP	6.5/10	533	Pb 1-e	6P	6.9/8
486	P 1-f	1.5RP	7.7/9	534	Pb 1-f	7P	7.8/6
487	P 1-g	3.5RP	8.8/8	535	Pb 1-g	8P	9/5?
488	P 1-h	2.5RP	9/4	536	Pb 1-h	?	>9/2?
489	P 2-a	4.5RP	2.4/2.6	537	Pb 2-a	2.0P	2.4/3.3
490	P 2-b	2.0RP	3.2/7.0	538	Pb 2-b	4.3P	3.6/8.0
491	P 2-c	2.0RP	4.2/7.2	539	Pb 2-c	5.0P	4.7/8.6
492	P 2-d	1.0RP	5.3/6.7	540	Pb 2-d	5.4P	5.6/8.0
493	P 2-e	2.0RP	6.0/6.4	541	Pb 2-e	6.3P	6.8/7.5
494	P 2-f	1.5RP	6.7/7.2	542	Pb 2-f	7P	7.3/6
495	P 2-g	3.0RP	8.4/8	543	Pb 2-g	8P	8.2/6
496	P 2-h	4RP	8.8/7	544	Pb 2-h	?9P	9/4
497	P 3-a	9P	2.4/2.4	545	Pb 3-a	3.0P	2.4/2.0
498	P 3-b	1.0RP	3.5/5.6	546	Pb 3-b	4.5P	3.6/6.0
499	P 3-c	1.0RP	4.7/5.8	547	Pb 3-c	5.0P	4.9/7.0
500	P 3-d	0.8RP	5.7/7.2	548	Pb 3-d	5.5P	6.3/6.4
501	P 3-e	2.0RP	6.5/5.4	549	Pb 3-e	6.3P	6.8/5.6
502	P 3-f	1.7RP	7.2/5.7	550	Pb 3-f	7P	7.7/5
503	P 3-g	2.0RP	7.8/6	551	Pb 3-g	8P	8.2/5
504	P 3-h	2.5RP	8.5/6	552	Pb 3-h	?8P	9/4
505	P 4-a	10P	2/1.5	553	Pb 4-a	1P	2.2/2.0
506	P 4-b	2.0RP	3.7/2.0	554	Pb 4-b	3.2P	3.5/3.5
507	P 4-c	0.7RP	4.2/4.0	555	Pb 4-c	4.5P	4.6/5.3
508	P 4-d	0.7RP	5.3/4.4	556	Pb 4-d	5.3P	5.7/5.3
509	P 4-e	1.2RP	6.2/4.0	557	Pb 4-e	6.0P	6.3/5.0
510	P 4-f	1.5RP	6.8/4.4	558	Pb 4-f	7P	7.6/4.7
511	P 4-g	1.8RP	8.2/4.7	559	Pb 4-g	8P	8.5/4
512	P 4-h	2.5RP	9/4	560	Pb 4-h	8P	9/2?
513	P 5-a	9.5P	2.0/1	561	Pb 5-a	3.5P	2.6/0.8
514	P 5-b	0.5RP	3.0/2.0	562	Pb 5-b	6.0P	3.3/2.6
515	P 5-c	0.7RP	4.1/3.8	563	Pb 5-c	6.3P	4.5/3.6
516	P 5-d	9.8P	4.9/3.6	564	Pb 5-d	7.0P	5.2/3.6
517	P 5-e	0.5RP	6.1/3.6	565	Pb 5-e	7.5P	6.1/3.5
518	P 5-f	0.5RP	6.9/3.6	566	Pb 5-f	7.0P	7.0/3.6
519	P 5-g	1.5RP	7.8/3.6	567	Pb 5-g	7P	7.8/4
520	P 5-h	2.0RP	9/4	568	Pb 5-h	?7P	8.7/4?
521	P 6-a	5P	2.2/1	569	Pb 6-a	8P	1.8/2.0
522	P 6-b	6.0P	3.2/1.5	570	Pb 6-b	7.2P	3.6/2.4
523	P 6-c	0.3RP	4.1/2.3	571	Pb 6-c	6.0P	4.4/2.5
524	P 6-d	1.2RP	4.8/2.3	572	Pb 6-d	7.0P	5.2/3.0
525	P 6-e	1.8RP	6.0/2.6	573	Pb 6-e	8.0P	6.3/3.0
526	P 6-f	10.0P	7.2/2.8	574	Pb 6-f	8.5P	7.0/3.5
527	P 6-g	1.8RP	7.8/3.5	575	Pb 6-g	1.0RP	7.8/3
528	P 6-h	1.3RP	8.8/3	576	Pb 6-h	?1RP	9/2?

TABLE II—*Continued*

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR—*Continued*

Plochere number	Plochere code	Munsell color	Plochere number	Plochere code	Munsell color
577	Bp 1–a	9.6PB 3.1/9.5	625	B 1–a	8.0PB 2.8/14
578	Bp 1–b	0.4P 4.2/10.0	626	B 1–b	8.0PB 3.8/13
579	Bp 1–c	0.5P 5.2/9.5	627	B 1–c	8.0PB 5.6/13
580	Bp 1–d	1.0P 6.3/8.5	628	B 1–d	7.5PB 6.4/12
581	Bp 1–e	1 3P 7.2/7.5	629	B 1–e	7.0PB 7.5/10
582	Bp 1–f	2P 8.3/6	630	B 1–f	6.7PB 8.5/7?
583	Bp 1–g	3P 9/3?	631	B 1–g	6.5PB 9.2/5?
584	Bp 1–h	? >9/1?	632	B 1–h	6PB >9/3?
585	Bp 2–a	9.6PB 3.1/7.5	633	B 2–a	8.0PB 3.0/9.0
586	Bp 2–b	0 5P 4.0/8.5	634	B 2–b	7.2PB 4.3/10.5
587	Bp 2–c	0.8P 5.2/5.6	635	B 2–c	7.0PB 5.8/9.5
588	Bp 2–d	1.8P 6.3/5.6	636	B 2–d	6.8PB 6.8/8.5
589	Bp 2–e	2.0P 7.4/5.3	637	B 2–e	6.5PB 7.6/7
590	Bp 2–f	2.5P 8.2/4	638	B 2–f	6.5PB 8.6/5
591	Bp 2–g	3P 9/2?	639	B 2–g	6.0PB 9.3/3?
592	Bp 2–h	? >9/1?	640	B 2–h	6PB <9/2?
593	Bp 3–a	9.6PB 2.7/3.6	641	B 3–a	6.0PB 2.8/4.5
594	Bp 3–b	0.4P 3.9/6.0	642	B 3–b	5.8PB 4.1/5.2
595	Bp 3–c	1.0P 5.2/5.6	643	B 3–c	5.5PB 5.3/6.0
596	Bp 3–d	2.0P 6.3/5.0	644	B 3–d	5.5PB 6.7/6.0
597	Bp 3–e	2.5P 7.2/4.7	645	B 3–e	5.5PB 7.7/6
598	Bp 3–f	2.5P 8.3/4	646	B 3–f	5PB 8.2/4
599	Bp 3–g	4P 9/2	647	B 3–g	5PB 9.1/3
600	Bp 3–h	?5P >9/1?	648	B 3–h	?5PB >9/1?
601	Bp 4–a	8.8PB 2.6/2.4	649	B 4–a	5.5PB 2.7/3.0
602	Bp 4–b	0.5P 3.6/3.0	650	B 4–b	5.5PB 3.9/4.0
603	Bp 4–c	2.0P 5.2/3.0	651	B 4–c	5.0PB 5.2/4.5
604	Bp 4–d	2.5P 5.8/3.6	652	B 4–d	5.0PB 6.0/4.0
605	Bp 4–e	2.0P 7.3/4.0	653	B 4–e	5.5PB 6.9/3.5
606	Bp 4–f	3P 8.3/3	654	B 4–f	5.5PB 8.2/3.0
607	Bp 4–g	3P 9/2	655	B 4–g	5PB 8.9/2
608	Bp 4–h	? >9/1?	656	B 4–h	?5PB >9/1?
609	Bp 5–a	8.5PB 2.5/0.7	657	B 5–a	5.0PB 2.3/2.0
610	Bp 5–b	9.0PB 3.7/1.5	658	B 5–b	4.5PB 3.8/3.5
611	Bp 5–c	0.4P 4.9/2.0	659	B 5–c	5.0PB 4.8/3.5
612	Bp 5–d	0.5P 6.2/2.4	660	B 5–d	5.5PB 5.9/3.0
613	Bp 5–e	1.5P 6.8/3.0	661	B 5–e	5.5PB 6.8/2.7
614	Bp 5–f	2.5P 7.8/2.0	662	B 5–f	6.0PB 7.7/2.5
615	Bp 5–g	3P 8.5/1	663	B 5–g	6PB 8.6/2
616	Bp 5–h	?3P 9.2/<1	664	B 5–h	6PB >9/1?
617	Bp 6–a	9.0PB 2.9/0.5	665	B 6–a	5PB 2.4/1.0
618	Bp 6–b	9.5PB 3.7/0.5	666	B 6–b	5.0PB 3.8/1.5
619	Bp 6–c	0.5P 5.2/0.8	667	B 6–c	4.2PB 5.2/2.0
620	Bp 6–d	1.0P 5.7/1.0	668	B 6–d	5.0PB 5.8/1.5
621	Bp 6–e	1.0P 6.9/1.3	669	B 6–e	5.5PB 6.7/1.5
622	Bp 6–f	1P 7.8/1.5	670	B 6–f	6.0PB 7.6/1.5
623	Bp 6–g	1.5P 8.5/1	671	B 6–g	6.5PB 8.6/1.5
624	Bp 6–h	1.5P 9.2/<1	672	B 6–h	?7PB >9/1

TABLE II—*Continued*

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR—*Continued*

Plochere number	Plochere code	Munsell color	Plochere number	Plochere code	Munsell color
673	Bg 1-a	7.8PB 2.3/10.5	721	Bgg 1-a	7.0PB 2.6/6.0
674	Bg 1-b	7.0PB 4.0/14.0	722	Bgg 1-b	4.5PB 3.3/12
675	Bg 1-c	6.0PB 4.8/12.5	723	Bgg 1-c	3.2PB 4.5/13
676	Bg 1-d	4.5PB 6.3/11.0	724	Bgg 1-d	2.5PB 5.4/12
677	Bg 1-e	4.0PB 7.5/9	725	Bgg 1-e	2.0PB 6.3/10
678	Bg 1-f	4PB 8.3/6	726	Bgg 1-f	1.0PB 7.5/8
679	Bg 1-g	3PB 9.0/3?	727	Bgg 1-g	1PB 8.6/6
680	Bg 1-h	?3PB >9/1?	728	Bgg 1-h	10B >9/3
681	Bg 2-a	7.0PB 2 5/6.0	729	Bgg 2-a	4.5PB 2.1/5.0
682	Bg 2-b	7.0PB 4.2/8.5	730	Bgg 2-b	3.0PB 3.1/8.5
683	Bg 2-c	6.8PB 5.1/9.0	731	Bgg 2-c	2.0PB 4.3/8.0
684	Bg 2-d	5 5PB 6.6/8.0	732	Bgg 2-d	2.0PB 5.1/8.0
685	Bg 2-e	5.5PB 7.3/5.3	733	Bgg 2-e	1.5PB 6.2/7.0
686	Bg 2-f	4.5PB 8.2/4	734	Bgg 2-f	1 0PB 6.9/6.5
687	Bg 2-g	4PB 9.0/3?	735	Bgg 2-g	1PB 7.8/4
688	Bg 2-h	?5PB >9/2?	736	Bgg 2-h	1PB 8.8/3
689	Bg 3-a	5.0PB 2.3/3.3	737	Bgg 3-a	1.3PB 2.5/2.5
690	Bg 3-b	5.0PB 3.9/5.6	738	Bgg 3-b	1.0PB 3.2/6.5
691	Bg 3-c	5.5PB 4.9/5.6	739	Bgg 3-c	1.3PB 4.3/7.5
692	Bg 3-d	5.0PB 6.3/5.5	740	Bgg 3-d	1.5PB 5.4/7.5
693	Bg 3-e	5.8PB 7.6/4.5	741	Bgg 3-e	0.5PB 6.3/6.5
694	Bg 3-f	6.0PB 8.1/4 0	742	Bgg 3-f	0.5PB 6.9/6.0
695	Bg 3-g	6.5PB 8.8/3.5	743	Bgg 3-g	0.5PB 7.8/5
696	Bg 3-h	7PB >9/2?	744	Bgg 3-h	1.3PB 8.4/4
697	Bg 4-a	5.0PB 2.3/2.4	745	Bgg 4-a	5PB 2.0/1.3
698	Bg 4-b	4.6PB 3.9/3.3	746	Bgg 4-b	10.0B 2.9/3.5
699	Bg 4-c	5.4PB 5.1/4.0	747	Bgg 4-c	9.0B 4.1/5.2
700	Bg 4-d	5.6PB 5.8/3.5	748	Bgg 4-d	9.0B 4.8/5.5
701	Bg 4-e	6.3PB 7.1/3.0	749	Bgg 4-e	9.5B 5.8/5.5
702	Bg 4-f	6.8PB 8.0/2.5	750	Bgg 4-f	0.5PB 7.2/6.0
703	Bg 4-g	7PB 8.8/2	751	Bgg 4-g	1.0PB 8.1/4.5
704	Bg 4-h	?8PB >9/1	752	Bgg 4-h	2PB 8.6/3
705	Bg 5-a	5.0PB 2.3/2.0	753	Bgg 5-a	6PB 2.2/0.7
706	Bg 5-b	4.5PB 3.8/2.5	754	Bgg 5-b	8B 2.7/1.3
707	Bg 5-c	4.0PB 4.8/2.7	755	Bgg 5-c	8.5B 3.9/3.5
708	Bg 5-d	4.5PB 5.8/2.5	756	Bgg 5-d	9.0B 4.8/4.0
709	Bg 5-e	6.0PB 6.7/1.8	757	Bgg 5-e	9.5B 6.3/4.0
710	Bg 5-f	6.5PB 7.5/2	758	Bgg 5-f	0.5PB 7.4/3.2
711	Bg 5-g	7PB 8.6/2	759	Bgg 5-g	1.5PB 7.7/3
712	Bg 5-h	?8PB >9/1?	760	Bgg 5-h	1PB 8.4/2
713	Bg 6-a	6PB 2.4/0.7	761	Bgg 6-a	2PB 2.3/0.5
714	Bg 6-b	5.5PB 3.7/1.5	762	Bgg 6-b	8.0B 3.0/1.3
715	Bg 6-c	5.5PB 5.2/2.0	763	Bgg 6-c	8.0B 4.2/2.0
716	Bg 6-d	6.2PB 5.8/2.0	764	Bgg 6-d	8.5B 4.8/3.5
717	Bg 6-e	7.0PB 6.8/2.0	765	Bgg 6-e	9.5B 6.1/3.0
718	Bg 6-f	7PB 7.2/1.5	766	Bgg 6-f	0.5PB 6.5/3.2
719	Bg 6-g	8PB 8.0/1.5	767	Bgg 6-g	1.0PB 7.5/3.0
720	Bg 6-h	9PB 8.6/1	768	Bgg 6-h	?2PB 8.5/2

TABLE II—*Continued*

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR—*Continued*

Plochere number	Plochere code	Munsell color		Plochere number	Plochere code	Munsell color	
769	BG 1–a	1.0PB	2.8/4.5	817	Gbb 1–a	4.0B	3.0/4.0
770	BG 1–b	9.0B	3.6/7.5	818	Gbb 1-b	3.0B	3.6/6.5
771	BG 1–c	6.0B	4.9/9	819	Gbb 1–c	2.0B	5.1/7.5
772	BG 1–d	7B	5 7/9?	820	Gbb 1–d	2B	5.8/8?
773	BG 1–e	7.5B	6.8/8.5	821	Gbb 1–e	2.5B	6.8/8
774	BG 1–f	8.0B	7.6/7	822	Gbb 1–f	3.0B	7.4/6.5
775	BG 1–g	8.5B	8.7/5	823	Gbb 1–g	3.0B	8.4/5
776	BG 1–h	9B	9/3	824	Gbb 1–h	3B	9/4
777	BG 2–a	2.5PB	2.4/3.0	825	Gbb 2–a	4.0B	2.8/2.5
778	BG 2–b	9.2B	3.4/6.5	826	Gbb 2–b	2.0B	3.3/6.0
779	BG 2–c	7.0B	4.6/8	827	Gbb 2–c	2.0B	4.4/6.8
780	BG 2–d	7.5B	5.4/8	828	Gbb 2–d	2.5B	5.7/7
781	BG 2–e	9.0B	6.5/7	829	Gbb 2–e	3.0B	6.6/6.5
782	BG 2–f	8.5B	7.3/7	830	Gbb 2–f	3.0B	7.4/5.5
783	BG 2–g	8.0B	8.0/5	831	Gbb 2–g	3.0B	7.7/4.5
784	BG 2–h	7B	9/3	832	Gbb 2–h	3B	8.6/4
785	BG 3–a	1.0PB	2.2/1.5	833	Gbb 3–a	6B	2.4/1.5
786	BG 3–b	8.0B	3.1/2.5	834	Gbb 3–b	3.0B	3.5/3.5
787	BG 3–c	7.5B	4.2/3.0	835	Gbb 3–c	1.5B	4.5/5.0
788	BG 3–d	8.0B	5.6/5.0	836	Gbb 3–d	3.5B	5.7/5.5
789	BG 3–e	8 5B	6.7/6.0	837	Gbb 3-e	4.0B	6.6/6.5
790	BG 3–f	8.0B	7.3/6.0	838	Gbb 3-f	3.3B	7.2/5.0
791	BG 3–g	7.5B	7.8/4.0	839	Gbb 3–g	4.2B	8.0/4.5
792	BG 3–h	7.0B	7.7/3.5	840	Gbb 3–h	6B	8.2/4
793	BG 4–a	4PB	2.1/1	841	Gbb 4–a	9B	2.4/0.5
794	BG 4–b	7.0B	3.0/2.0	842	Gbb 4–b	3.0B	3.0/1.5
795	BG 4–c	7.0B	3.9/3.5	843	Gbb 4–c	3.0B	4.2/3.5
796	BG 4–d	6.5B	4.6/4.0	844	Gbb 4–d	2.5B	5.1/4.0
797	BG 4–e	6.0B	6.0/4.0	845	Gbb 4–e	2.0B	6.2/3.5
798	BG 4–f	8.5B	7.1/4.5	846	Gbb 4-f	4.5B	7.8/3.5
799	BG 4–g	9.5B	8.1/3.5	847	Gbb 4–g	4.5B	8.2/2.5
800	BG 4–h	?8B	8.4/2.5	848	Gbb 4–h	?4B	8.9/2
801	BG 5–a	4PB	2.3/0.5	849	Gbb 5–a	2PB	1.8/0.5
802	BG 5–b	9B	3.1/2.5	850	Gbb 5–b	4.0B	2.8/1.3
803	BG 5–c	7.0B	4.0/2.5	851	Gbb 5–c	3.5B	3.8/3.0
804	BG 5–d	6.0B	5.3/2.5	852	Gbb 5–d	3.0B	5.1/3.5
805	BG 5–e	5.5B	6.3/2.0	853	Gbb 5–e	1.5B	6.1/3.0
806	BG 5–f	6.5B	6.8/2.0	854	Gbb 5–f	3.0B	6.7/3.0
807	BG 5–g	9.0B	7.9/2	855	Gbb 5–g	4.0B	7.7/2.5
808	BG 5–h	9.5B	8.3/2	856	Gbb 5–h	5B	8.2/2.0
809	BG 6–a	4PB	2.4/0.4	857	Gbb 6–a	?5PB	1.5/0.4?
810	BG 6–b	9.0B	3.1/2.4	858	Gbb 6–b	?3B	2.6/0.8
811	BG 6–c	6.5B	4.0/2.0	859	Gbb 6–c	4B	4.4/1.6
812	BG 6–d	7.5B	5.1/1.5	860	Gbb 6–d	3B	5.3/2.4
813	BG 6–e	8.0B	6.3/1.5	861	Gbb 6–e	3B	6.5/2.0
814	BG 6–f	9.0B	6.8/1.5	862	Gbb 6-f	4B	6.9/1.6
815	BG 6–g	1.0PB	7.7/1	863	Gbb 6–g	6B	7.7/1.3
816	BG 6–h	0.5PB	8.2/1	864	Gbb 6–h	10B	8.4/1

TABLE II—*Continued*

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR—*Continued*

Plochere number	Plochere code	Munsell color	Plochere number	Plochere code	Munsell color
865	Gb 1–a	9.0BG 3.2/6.0	913	G 1–a	3.5BG 3.2/5.5
866	Gb 1–b	7.0BG 4.2/6.5	914	G 1–b	3.0BG 4.5/6.0
867	Gb 1–c	7.0BG 5.2/8	915	G 1–c	3.0BG 5.4/8
868	Gb 1–d	8.0BG 5.7/9	916	G 1–d	2.5BG 6.2/9?
869	Gb 1–e	9BG 6.7/9?	917	G 1–e	2BG 7.3/8
870	Gb 1–f	8BG 7.9/7?	918	G 1–f	3BG 8.3/5
871	Gb 1–g	9BG 8.8/5?	919	G 1–g	4BG 9.0/4
872	Gb 1–h	?10BG >9/2	920	G 1–h	?4BG >9/2
873	Gb 2–a	9.0BG 2.8/3.0	921	G 2–a	6.0BG 2.8/3.6
874	Gb 2–b	9.0BG 4.1/6.0	922	G 2–b	3.5BG 4.0/5.6
875	Gb 2–c	8.0BG 4.9/6.0	923	G 2–c	4.0BG 5.1/7.0
876	Gb 2–d	7.5BG 5.7/8	924	G 2–d	3.5BG 5.8/8
877	Gb 2–e	8.8BG 6.6/8?	925	G 2–e	4.0BG 6.7/8?
878	Gb 2–f	8BG 7 6/6?	926	G 2–f	3.0BG 7.5/7?
879	Gb 2–g	8BG 8.3/4.5	927	G 2–g	4BG 8.3/4
880	Gb 2–h	9BG 9.2/3?	928	G 2–h	5BG 9.0/2
881	Gb 3–a	10BG 2.7/1.5	929	G 3–a	9BG 2.6/2.0
882	Gb 3–b	8.5BG 3 6/3.5	930	G 3–b	5.0BG 3.7/4.4
883	Gb 3–c	8.5BG 4.5/4.5	931	G 3–c	4.0BG 4.6/5.0
884	Gb 3–d	9.0BG 5.6/5.5	932	G 3–d	3.8BG 5.4/5.5
885	Gb 3–e	9.0BG 6.5/6.0	933	G 3–e	4.5BG 6.0/6.0
886	Gb 3–f	8.8BG 7.7/5.0	934	G 3–f	6.0BG 7.4/6.0
887	Gb 3–g	8.5BG 8.3/4	935	G 3–g	6.5BG 8.4/4.0
888	Gb 3–h	?8BG 8.9/4?	936	G 3–h	7BG 8.6/3.0
889	Gb 4–a	1.5B 2.1/1.3	937	G 4–a	1B 2 4/1.0
890	Gb 4–b	0.5B 3.6/2.8	938	G 4–b	6.2BG 3.5/2.5
891	Gb 4–c	0.5B 4.7/3.5	939	G 4–c	5.5BG 4.5/3.5
892	Gb 4–d	9.0BG 5.2/4.4	940	G 4–d	6.0BG 5.2/3.5
893	Gb 4–e	9.5BG 6.2/4.0	941	G 4–e	6.8BG 6.2/4.0
894	Gb 4–f	10.0BG 7.4/3.5	942	G 4–f	8.0BG 7.8/3.5
895	Gb 4–g	1.0B 8.4/3.5	943	G 4–g	9BG 8.4/2.5
896	Gb 4–h	1B 9.0/3	944	G 4–h	9BG 8.8/2
897	Gb 5–a	4B 2.0/1 0	945	G 5–a	2B 2.1/0.5
898	Gb 5–b	2.0B 3.3/2.0	946	G 5–b	7BG 3.8/1.5
899	Gb 5–c	1.0B 4.3/3.0	947	G 5–c	6.0BG 4.4/2.0
900	Gb 5–d	1.0B 5.2/3.0	948	G 5–d	5.5BG 5.2/2.5
901	Gb 5–e	1.3B 6.3/2.8	949	G 5–e	5.8BG 6.1/2.7
902	Gb 5–f	1.5B 7.4/2.8	950	G 5–f	6.0BG 6.8/3.0
903	Gb 5–g	2.0B 8.4/2.0	951	G 5–g	7.5BG 7.6/2.5
904	Gb 5–h	2.0B 8 7/1.5?	952	G 5–h	8.5BG 8.2/2.0
905	Gb 6–a	?6B 2.3/0.5	953	G 6–a	5B 2.0/0.4?
906	Gb 6–b	?2B 3.3/1.0	954	G 6–b	1.0B 3.3/1.0
907	Gb 6–c	1.5B 4.3/1.5	955	G 6–c	9.5BG 4.2/1.6
908	Gb 6–d	1.0B 5.2/2.0	956	G 6–d	9.0BG 5.1/2.0
909	Gb 6–e	0.5B 6.0/2.0	957	G 6–e	10.0BG 6.2/2.0
910	Gb 6–f	10BG 6.7/2.0	958	G 6–f	9.5BG 7.2/1.6
911	Gb 6–g	1B 7.3/1.5	959	G 6–g	1.0B 7.7/1.5
912	Gb 6–h	2B 8.2/1.5	960	G 6–h	2B 8.4/1

TABLE II—*Continued*

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR—*Continued*

Plochere number	Plochere code	Munsell color	Plochere number	Plochere code	Munsell color
961	Gy 1–a	2.0BG 3.1/7	1009	Gyy 1–a	5.0G 4.3/11?
962	Gy 1–b	9.5G 4.6/8	1010	Gyy 1–b	4.5G 5.4/12?
963	Gy 1–c	9.0G 5.5/9?	1011	Gyy 1–c	4.0G 6.1/12?
964	Gy 1–d	9.0G 6.2/9?	1012	Gyy 1–d	4.0G 6.7/10?
965	Gy 1–e	0.5BG 6.8/9?	1013	Gyy 1–e	4.5G 7.5/8.0
966	Gy 1–f	1.0BG 8.2/8?	1014	Gyy 1–f	5.5G 8.4/7
967	Gy 1–g	1 5BG 8.6/6?	1015	Gyy 1–g	6.0G 9/4
968	Gy 1–h	2BG >9/4?	1016	Gyy 1–h	?7G >9/2
869	Gy 2–a	1 0BG 3.0/4.0	1017	Gyy 2–a	4.5G 3.3/6
970	Gy 2–b	10.0G 4.6/5.6	1018	Gyy 2–b	4.5G 4.8/8.0
971	Gy 2–c	0.8BG 5.3/6.5	1019	Gyy 2–c	4.5G 5.8/7.5
972	Gy 2–d	1.0BG 6.0/7.0	1020	Gyy 2–d	4.2G 6.8/7.0
973	Gy 2–e	1.0BG 6.8/6.5	1021	Gyy 2–e	5.5G 7.8/7.0
974	Gy 2–f	1.5BG 7.6/6?	1022	Gyy 2–f	5.7G 8.3/6.0
975	Gy 2–g	?2BG 8.8/4	1023	Gyy 2–g	6G 8.9/4
976	Gy 2–h	?5BG >9/1?	1024	Gyy 2–h	7G >9/2
977	Gy 3–a	2 5BG 2 7/2.0	1025	Gyy 3–a	7.0G 2.9/2.2
978	Gy 3–b	0.8BG 3.9/3.5	1026	Gyy 3–b	6.3G 3.9/3.6
979	Gy 3–c	1.5BG 4.8/4.5	1027	Gyy 3–c	6.5G 5.2/4.0
980	Gy 3–d	2.5BG 5.4/5.0	1028	Gyy 3–d	6.0G 5.9/4.5
981	Gy 3–e	3.5BG 6.2/5.0	1029	Gyy 3–e	5.5G 6.9/4.0
982	Gy 3–f	3.5BG 7.3/5	1030	Gyy 3–f	6.5G 8.0/3.5
983	Gy 3–g	3BG 8.4/4	1031	Gyy 3–g	6.5G 8.5/2.5
984	Gy 3–h	?5BG >9/2?	1032	Gyy 3–h	7G 9/2
985	Gy 4–a	?3BG 2.3/1.6	1033	Gyy 4–a	8G 2.3/2.0
986	Gy 4–b	1.0BG 3.7/2.5	1034	Gyy 4–b	6.0G 3.8/2.5
987	Gy 4–c	3.5BG 4.2/3.5	1035	Gyy 4–c	6.0G 5.1/3.0
988	Gy 4–d	3.8BG 5.2/3.5	1036	Gyy 4–d	6 5G 5 7/2.7
989	Gy 4–e	3.5BG 6.0/3.2	1037	Gyy 4–e	7.0G 6.6/3.0
990	Gy 4–f	4.0BG 7.4/3.0	1038	Gyy 4–f	7.5G 7.8/2.7
991	Gy 4–g	5.0BG 8 6/2.4	1039	Gyy 4–g	7.5G 8.6/2 0
992	Gy 4–h	7BG 9.0/2	1040	Gyy 4–h	8G 9.0/1.5?
993	Gy 5–a	7BG 1.8/1.5	1041	Gyy 5–a	9G 2.4/1.0
994	Gy 5–b	3.8BG 3.2/1.6	1042	Gyy 5–b	8.5G 3.5/1.5
995	Gy 5–c	4.0BG 4.4/2.8	1043	Gyy 5–c	8.3G 4.8/2.0
996	Gy 5–d	4.5BG 5.3/2.5	1044	Gyy 5–d	10.0G 5.1/2.0
997	Gy 5–e	4.5BG 6.2/2.4	1045	Gyy 5–e	10.0G 6.6/1.5
998	Gy 5–f	5.5BG 6.5/2.5	1046	Gyy 5–f	1.0BG 6.9/1.5
999	Gy 5–g	6.0BG 7.7/2.5	1047	Gyy 5–g	2BG 7.8/1.3
1000	Gy 5–h	7BG 8.4/2	1048	Gyy 5–h	2BG 8.6/1
1001	Gy 6–a	?10BG 2 3/1	1049	Gyy 6–a	4BG 2.5/0.5
1002	Gy 6–b	6BG 3.4/1.5	1050	Gyy 6–b	2BG 3.7/1.0
1003	Gy 6–c	6.5BG 4.4/2.0	1051	Gyy 6–c	2BG 4.9/1.0
1004	Gy 6–d	6.8BG 5.2/2.4	1052	Gyy 6–d	3BG 5.6/0.7
1005	Gy 6–e	6.5BG 6.1/2.4	1053	Gyy 6–e	?4BG 6.4/0.7
1006	Gy 6–f	7.0BG 6.8/2.0	1054	Gyy 6–f	?4BG 6.7/0.5
1007	Gy 6–g	9.0BG 7.7/2 0	1055	Gyy 6–g	5BG 7.7/0.5
1008	Gy 6–h	10BG 8.4/1.5	1056	Gyy 6–h	?7BG 8.5/0.3

TABLE II—*Continued*

Comparison of Plochere colors with Munsell book of color—*Continued*

Plochere number	Plochere code	Munsell color	Plochere number	Plochere code	Munsell color
1057	GY 1–a	3.8G 4.8/12?	1105	Ygg 1–a	9GY 6.3/14?
1058	GY 1–b	2.5G 5.8/12	1106	Ygg 1–b	9.5GY 7.0/12?
1059	GY 1–c	2.0G 6.7/11	1107	Ygg 1–c	9.0GY 7.7/11
1060	GY 1–d	2.0G 7.3/10	1108	Ygg 1–d	8.0GY 8.5/9.0
1061	GY 1–e	1.8G 8.2/9.0	1109	Ygg 1–e	7.5GY 8.8/7.5
1062	GY 1–f	1.3G 8.8/7.0	1110	Ygg 1–f	6.5GY 9.2/5.0
1063	GY 1–g	1G >9/4	1111	Ygg 1–g	5GY >9/4
1064	GY 1–h	?10GY >9/2	1112	Ygg 1–h	?5GY >9/1?
1065	GY 2–a	2.5G 3.8/6.0	1113	Ygg 2–a	9.5GY 5.4/10.5
1066	GY 2–b	2.0G 5.1/7.0	1114	Ygg 2–b	9.0GY 6.5/9.0
1067	GY 2–c	1.5G 6.2/6.7	1115	Ygg 2–c	7.8GY 7.1/7.6
1068	GY 2–d	1.3G 7.0/5.6	1116	Ygg 2–d	7.2GY 7.9/7.2
1069	GY 2–e	1.3G 8.0/6.0	1117	Ygg 2–e	6.5GY 8.7/6.5
1070	GY 2–f	1.0G 8.5/4.0	1118	Ygg 2–f	6.0GY 9.0/5.0
1071	GY 2–g	1G 9.0/3	1119	Ygg 2–g	5GY >9/4?
1072	GY 2–h	?10GY >9/1	1120	Ygg 2–h	?5GY >9/1?
1073	GY 3–a	2.5G 3.1/3.0	1121	Ygg 3–a	8.0GY 4.1/6.5
1074	GY 3–b	1.0G 4.8/4.4	1122	Ygg 3–b	7.2GY 5.2/6.0
1075	GY 3–c	1.0G 5.8/4.4	1123	Ygg 3–c	7.0GY 6.3/5.5
1076	GY 3–d	0.5G 6.4/3.6	1124	Ygg 3–d	6.8GY 6.8/5.2
1077	GY 3–e	0.5G 7.0/3.5	1125	Ygg 3–e	6.0GY 7.8/5.0
1078	GY 3–f	10.0GY 8.3/2.5	1126	Ygg 3–f	5.5GY 8.5/4.0
1079	GY 3–g	10GY 9/1.5	1127	Ygg 3–g	5.0GY 9.2/3
1080	GY 3–h	?10GY >9/1	1128	Ygg 3–h	?5GY >9/1?
1081	GY 4–a	3.5G 2.7/1.5	1129	Ygg 4–a	7.5GY 3.4/4.5
1082	GY 4–b	1.0G 3.8/3.2	1130	Ygg 4–b	7.0GY 4.8/4.5
1083	GY 4–c	1.0G 5.0/3.5	1131	Ygg 4–c	6.0GY 5.7/4.0
1084	GY 4–d	0.5G 6.0/3.5	1132	Ygg 4–d	5.5GY 6.4/3.5
1085	GY 4–e	10.0GY 7.0/3.0	1133	Ygg 4–e	5.0GY 7.3/3.2
1086	GY 4–f	1.0G 8.0/2.0	1134	Ygg 4–f	4.5GY 8.5/3.0
1087	GY 4–g	2.5G 8.8/1.0	1135	Ygg 4–g	4.5GY 9.0/2.5
1088	GY 4–h	?3G >9/0.7?	1136	Ygg 4–h	?4GY >9/1
1089	GY 5–a	2.5G 2.3/0.8	1137	Ygg 5–a	7.5GY 3.1/2.0
1090	GY 5–b	2.0G 3.5/1.5	1138	Ygg 5–b	7.0GY 3.8/2.8
1091	GY 5–c	1.3G 4.9/1.6	1139	Ygg 5–c	6.5GY 5.3/3.0
1092	GY 5–d	0.8G 5.8/2.0	1140	Ygg 5–d	5.8GY 6.2/2.8
1093	GY 5–e	0.5G 6.9/1.5	1141	Ygg 5–e	5.5GY 7.2/2.5
1094	GY 5–f	10.0GY 7.6/1.0	1142	Ygg 5–f	5.0GY 7.7/2.5
1095	GY 5–g	10GY 8.0/0.8	1143	Ygg 5–g	5GY 8.1/1.5
1096	GY 5–h	?10GY 8.5/0.5	1144	Ygg 5–h	?4GY 8.7/1
1097	GY 6–a	3G 2.1/0.5	1145	Ygg 6–a	6GY 2.5/1.5
1098	GY 6–b	2G 3.8/1.0	1146	Ygg 6–b	6.0GY 3.9/2.0
1099	GY 6–c	1G 4.6/0.8	1147	Ygg 6–c	6.5GY 5.0/1.8
1100	GY 6–d	1G 5.7/1.0	1148	Ygg 6–d	6.5GY 5.4/1.8
1101	GY 6–e	10GY 6.6/1.0	1149	Ygg 6–e	5.8GY 6.9/1.6
1102	GY 6–f	10GY 7.2/1.0	1150	Ygg 6–f	5.5GY 7.3/1.2
1103	GY 6–g	?10GY 7.8/0.7	1151	Ygg 6–g	5GY 8.0/1.0
1104	GY 6–h	?10GY 8.5/0.5	1152	Ygg 6–h	?4GY 8.6/0.5

TABLE II—*Concluded*

COMPARISON OF PLOCHERE COLORS WITH MUNSELL BOOK OF COLOR—*Concluded*

Plochere number	Plochere code	Munsell color	Plochere number	Plochere code	Munsell color
1153	Yg 1–a	6.5GY 7.6/13	1201	YYg 1–a	2.0GY 8.0/10
1154	Yg 1–b	4.5GY 8.5/11	1202	YYg 1–b	1.5GY 8.8/10.0
1155	Yg 1–c	3.5GY 8.9/10	1203	YYg 1–c	1.0GY 8.9/9.0
1156	Yg 1–d	2.5GY 9.2/9	1204	YYg 1–d	10Y 9.0/8
1157	Yg 1–e	2GY >9/7	1205	YYg 1–e	10Y 9.1/7?
1158	Yg 1–f	1GY >9/6	1206	YYg 1–f	9Y 9.2/6?
1159	Yg 1–g	1GY >9/3	1207	YYg 1–g	9Y >9/4?
1160	Yg 1–h	?10Y >9/1	1208	YYg 1–h	8Y >9/1?
1161	Yg 2–a	5.8GY 7.0/11.0	1209	YYg 2–a	1.5GY 7.4/8.0
1162	Yg 2–b	4.5GY 7.8/8.0	1210	YYg 2–b	0.5GY 8.0/8.0
1163	Yg 2–c	3.0GY 8.3/8.0	1211	YYg 2–c	10.0Y 8.8/8
1164	Yg 2–d	2.5GY 8.9/6.5	1212	YYg 2–d	9.0Y 9/7
1165	Yg 2–e	2.0GY 9.2/6.0	1213	YYg 2–e	9Y >9/6
1166	Yg 2–f	1.5GY >9/5	1214	YYg 2–f	9Y >9/4
1167	Yg 2–g	1GY >9/4?	1215	YYg 2–g	8Y >9/2
1168	Yg 2–h	10Y >9/1?	1216	YYg 2–h	?7Y >9/1
1169	Yg 3–a	4.5GY8 5.9/8.	1217	YYg 3–a	2.0GY 5.8/7.6
1170	Yg 3–b	3.2GY 7.0/8.0	1218	YYg 3–b	1.5GY 6.8/7.0
1171	Yg 3–c	2.5GY 7.8/7.0	1219	YYg 3–c	1.8GY 7.8/7.0
1172	Yg 3–d	2.5GY 8.3/6.0	1220	YYg 3–d	1.5GY 8.4/6.7
1173	Yg 3–e	2.0GY 9.0/5.0	1221	YYg 3–e	0.5GY 8.9/6.0
1174	Yg 3–f	1.5GY >9/4.5	1222	YYg 3–f	10Y >9/5
1175	Yg 3–g	1GY >9/4	1223	YYg 3–g	10Y >9/4
1176	Yg 3–h	?10Y >9/1?	1224	YYg 3–h	10Y >9/3
1177	Yg 4–a	4.5GY 4.6/4.5	1225	YYg 4–a	4.0GY 4.6/5.5
1178	Yg 4–b	4.0GY 5.5/5.5	1226	YYg 4–b	3.0GY 5.4/6.0
1179	Yg 4–c	3.0GY 6.5/5.5	1227	YYg 4–c	2.5GY 6.6/5.0
1180	Yg 4–d	2.5GY 7.2/5.0	1228	YYg 4–d	1.8GY 7.2/5.0
1181	Yg 4–e	2.0GY 7.8/4.5	1229	YYg 4–e	1.8GY 7.9/4.7
1182	Yg 4–f	2.0GY 8.1/4.5	1230	YYg 4–f	1.0GY 8.9/3
1183	Yg 4–g	2GY 8.6/3.5	1231	YYg 4–g	1GY >9/3?
1184	Yg 4–h	1GY >9/1?	1232	YYg 4–h	10Y >9/2?
1185	Yg 5–a	6.0GY 3.3/4.0	1233	YYg 5–a	5.0GY 3.5/4.4
1186	Yg 5–b	5.0GY 4.6/3.5	1234	YYg 5–b	4.0GY 4.6/4.0
1187	Yg 5–c	4.5GY 5.5/3.5	1235	YYg 5–c	4.0GY 5.7/3.6
1188	Yg 5–d	4.0GY 6.5/3.5	1236	YYg 5–d	3.2GY 6.5/3.5
1189	Yg 5–e	3.3GY 7.4/3.0	1237	YYg 5–e	2.5GY 7.3/3.5
1190	Yg 5–f	3.0GY 7.8/2.8	1238	YYg 5–f	2.0GY 7.8/3.0
1191	Yg 5–g	2.5GY 8.1/2.5	1239	YYg 5–g	1.5GY 8.5/2.4
1192	Yg 5–h	2GY 8.8/2	1240	YYg 5–h	1GY 9.0/2
1193	Yg 6–a	6.5GY 2.7/1.5	1241	YYg 6–a	6.0GY 2.7/2.0
1194	Yg 6–b	5.0GY 3.9/2.0	1242	YYg 6–b	5.0GY 3.9/2.5
1195	Yg 6–c	4.5GY 5.1/2.4	1243	YYg 6–c	4.2GY 5.3/2.0
1196	Yg 6–d	4.5GY 6.0/2.4	1244	YYg 6–d	4.0GY 6.2/2.0
1197	Yg 6–e	3.5GY 6.9/1.6	1245	YYg 6–e	3.0GY 7.0/1.6
1198	Yg 6–f	3.0GY 7.3/1.6	1246	YYg 6–f	2.5GY 7.4/1.5
1199	Yg 6–g	2.5GY 7.9/1.2	1247	YYg 6–g	2.0GY 8.1/1.2
1200	Yg 6–h	2GY 8.5/1	1248	YYg 6–h	?1GY 8.9/1

and the occasional shifts of hue, produced by the addition of black* or other modifying pigments. It is clear that the hue changes were not intended, but arose from the mixture of pigments. The marked changes following numbers 1, 49, 97, and 145 appear to be due to the addition of raw sienna.

The hues are fairly regularly distributed with the exception of a large hiatus in the region of 7.5 P, which is filled in to some extent in the low chroma series. Probably this hue is not much used nowadays in higher chromas. There is also a break at 10Y which is very clearly marked except in the series of highest chroma (1201–1208 and 1–8).

A distinct impression was felt during the matching that the hues between RP and G through B tended to go towards blue with the addition of black. This is confirmed by Fig. 1.

A similar polar plot of value against hue was prepared but is not reproduced. It shows the same general features, but less clearly.

Two of the blocks, beginning with 625 and 673, are very similar as far as their leading colors are concerned, but produce delicately different results when mixed with white, so that their separate existence may be desirable from the standpoint of the decorator. The writer has no desire to go at this time into the elusive subject of pigment mixture, but colors 681–688 and 721–728 offer a most interesting study. The leading colors of these series are very nearly alike, their color difference measured on the Hunter reflectometer (4) being only 2.2 judd. Mixture with white, however, produces widely different tints, the color difference between 722 and 682 for example, being 18 judd. The course of the two series in value and chroma is indicated in Fig. 2, in which the small circles indicate the series 721–728, the black dots the series 681–688.

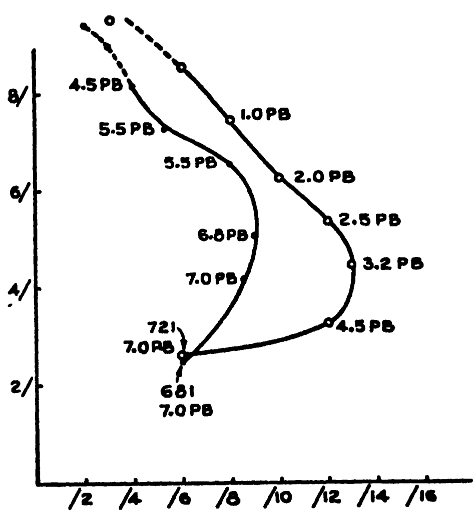

FIG. 2. *Value and chroma of two series of which the leading colors are very nearly alike.*

* *It is stated (8, p. 9) that "as there is no such color as pure black we had a color mixed which we term black and which is called black in this system."*

The Munsell hue of each sample is also indicated in the figure. The reason for this behavior is seen in the spectral reflectance curves of Fig. 3, which show large differences at both ends of the spectrum.

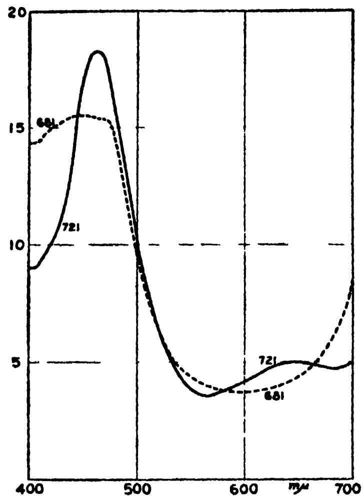

FIG. 3. *Spectral reflectance of the leading colors in the series shown in Fig. 2.*

The method of plotting used in Fig. 2 discloses great differences of behavior when different colors are mixed with white. In Fig. 4*a* the entire block 721–768 is set out, and it will be seen that the addition of white at first increases the chroma, with little effect on value, the curves exhibiting a maximum. The yellow-greens 1105–1152, on the other hand (see Fig. 4*b*), are reduced in chroma by any addition of white, except where they have been largely mixed with black (1137–1144, 1145–1152). Figs. 4*c* and 4*d* show blocks intermediate in behavior and a rather irregular block is shown in Fig. 4*e*.

The addition of white naturally leads to progressive hue changes. In Fig. 5 the hues of the leading series in each block are plotted for each Plochere value level. There is some regularity in the behavior of the hues as white is added, the series in the neighborhood of 8Y and 2.5RP tending to converge to these hues, while other series diverge from 8PB, 6R, and (less definitely) 2.5G. It may be no more than a coincidence that 8Y and 8PB, also 2.5RP and 2.5G, are complementary pairs, especially since nothing appears at the complementary of 6R. It will also be noted that levels d and e provide a fairly uniform range of hues in the leading series of the blocks.

The fourth series of each block has been similarly plotted in Fig. 6. The points of divergence and convergence persist, though less marked, the one in the vicinity of 2.5RP and 2.5G being rather diffuse. At this chroma level the series beginning with 649 and 697 differ by little more than the probable error of matching.

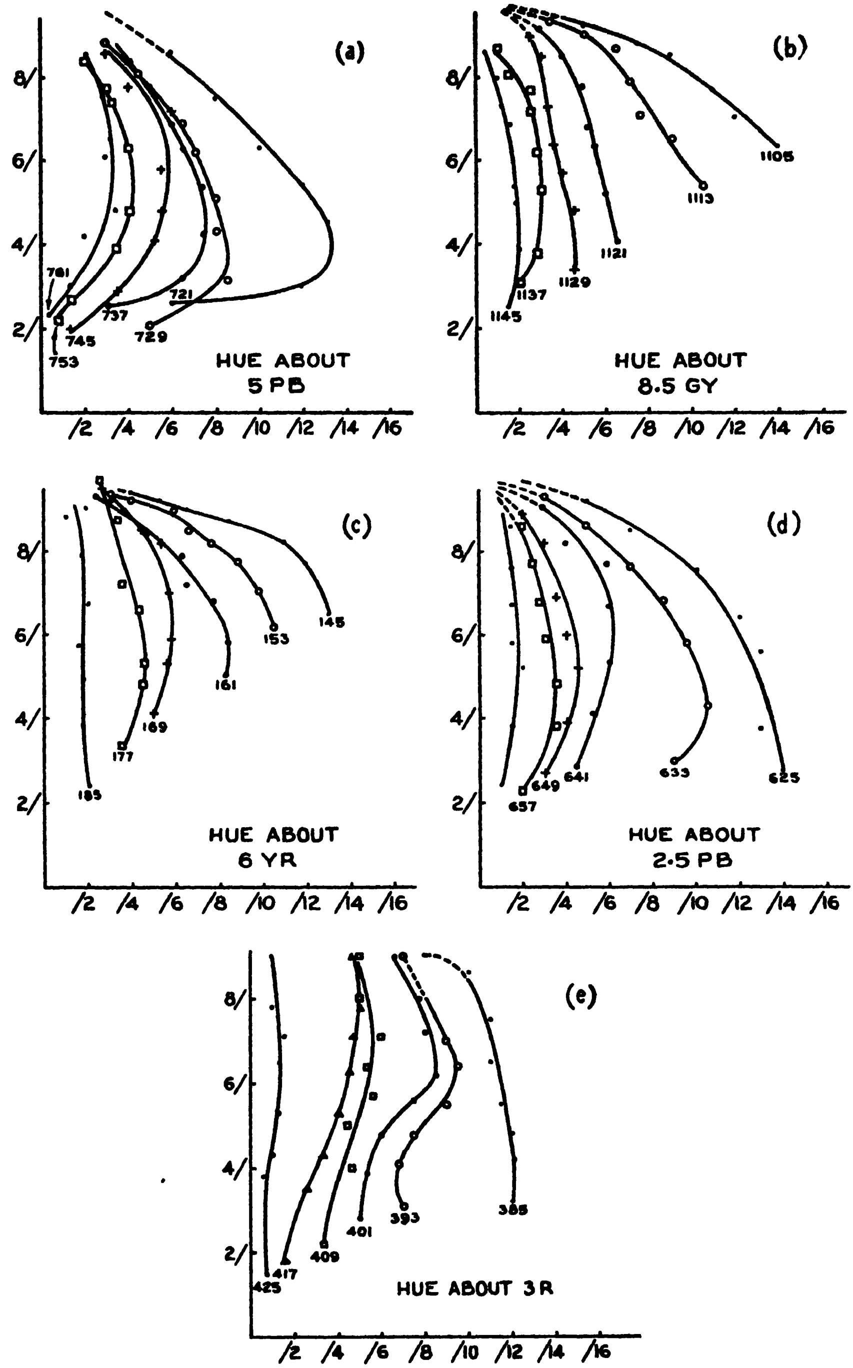

FIG. 4. *Value and chroma. (a) A block of colors in which the addition of white at first raises chroma markedly; (b) one in which it lowers chroma except in the series of lowest saturation; (c) and (d) blocks intermediate in behavior; (e) one with irregular changes in chroma.*

Evaluation of the Plochere System

In general the Plochere system seems very suitable for its purpose. Nearly all the samples have very uniform matte surfaces, only one being noted as significantly nonuniform over its area. Some colors of low value show slight

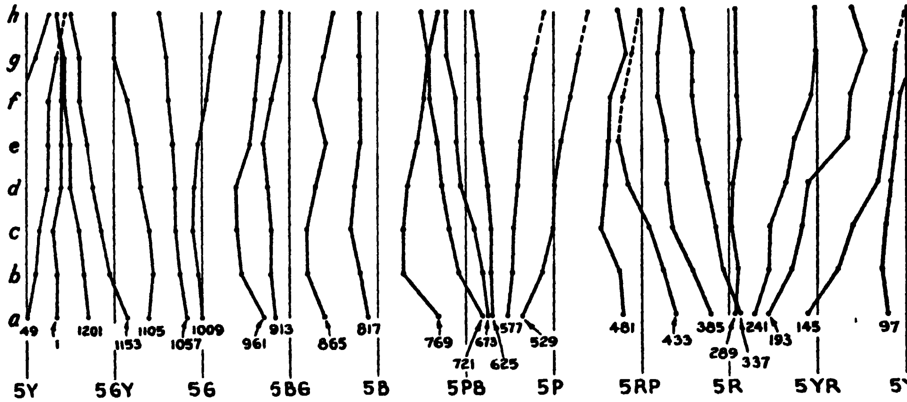

FIG. 5. *Hue changes with addition of white for the leading series of the 26 blocks. The ordinates are the Plochere value levels.*

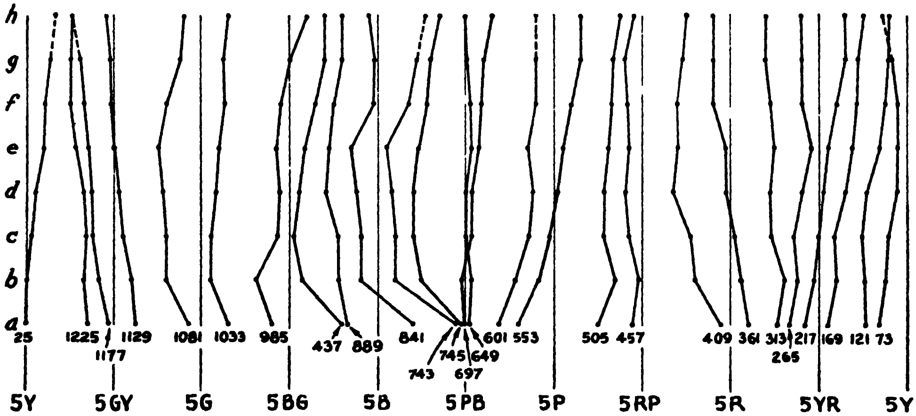

FIG. 6. *Hue changes with addition of white for the fourth series of each block.*

bronzing, others are slightly glossy; but these defects are common to other systems using painted samples. The large size of the cards is a distinct advantage to the user.

Some of the blocks are probably slightly fluorescent. This may be inevitable in a system which covers so wide a range of chroma and value. None, however, seem to fluoresce notably in the near ultraviolet from a standard "black light" lamp.

Many of the light tints are very difficult to distinguish from others of similar value in the same region of hue, and at first sight the system might be criticized as being redundant. Such criticism would have to ignore the stated purpose

of the system, which is to show the colors obtained by mixing certain chromatic pigments with black and white in stated proportions. The "rectangular" arrangement is probably the best for this purpose, though not necessary for the study of color harmony.

A more valid criticism concerns the irregularity in hue, especially the large hiatus in the purple, which might well be filled in future editions. Not very much harm would be done by omitting the present Bg block (673-720), and a new one beginning near 2 5P might well replace it. On the other side of the hue circle, the blocks 1201–1248, 1–48, 49–96, and 97–144 might well be modified to keep them more constant in hue

These are minor defects, and detract only a little from the general usefulness of the Plochere System in the field for which it is designed. It may further be suggested that colorimetrists and other color workers will find the Plochere cards a useful source of well made chromatic surfaces for any purpose where standardized samples are not needed

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DIAMOND DRILL HOLE G-M COUNTER[1]

BY K. FELDMAN[2] AND G. M. WRIGHT[2]

Abstract

A portable instrument for making gamma-ray surveys of diamond drill holes to depths of 1000 ft. is described. The circuit is given in detail.

This instrument was designed for detecting gamma-rays in diamond drill holes of diameter not less than 1.25 in. to depths of 1000 ft. It consists of battery-operated electronic circuits with a G-M tube at the end of a cable, and indicates the counting rate on a rate meter and a loudspeaker. The chassis housing the electronic circuits is fastened to the side of the reel carrying the cable, and rotates with it. The reel is mounted on a portable framework designed to be carried by two men.

Briefly, the circuit works as follows. Each "count" from the G-M tube, attenuated by the cable, is amplified and actuates a trigger circuit. The square pulse thus generated is modulated by a neon oscillator. This modulated pulse, amplified by the power amplifier, gives a note in the loudspeaker and actuates the rate meter.

The Electronic Circuit

The early models of diamond drill hole counter apparatus developed at the National Research Laboratories, Ottawa, consisted of simple circuits similar to those used in other portable counters, with the addition of a probe at the end of a long cable. This probe contained the G-M tube and a suitable amplifier circuit (1). Field experience showed that various modifications were desirable, the most important of which was the elimination of the amplifier circuit in the probe since it frequently gave trouble and was very inconvenient to service.

In the present instrument, these modifications have been made. Only the more unusual features will be described in detail.

(a) G-M Tube and Cable

The G-M tube is of the self-quenching type, requiring an operating voltage of about 1000 v. Both glass and all-metal types have been used, as discussed in a later section on probes.

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[2] *Physicist.*

When sufficient amplification is provided at the upper end of the cable, it is found satisfactory to omit the preamplifier in the probe. This not only avoids the trouble previously mentioned but also greatly simplifies the construction and makes it possible to permanently seal the probe. It also eliminates practically all drain on the high voltage circuit, and makes possible the use of a cable having only two conductors of negligible current-carrying capacity.

(b) High Voltage Circuit

The high voltage circuit (V1 and V2, Fig. 1) is of the same type as that previously discussed (1). However, since considerable amplification of the counts is necessary, and since the interconductor capacitance of the cable feeds the ripple from the high voltage circuit directly to the amplifier, it is necessary to add the two-stage filter. It is also necessary to exercise care in wiring, to avoid placing input leads where they might pick up ripple from the high voltage circuit.

(c) Amplifier and Trigger Circuit

The two-stage voltage amplifier (V3 and V4) has a gain of about 2500. The grid resistor in the first stage also serves as the load resistor for the G-M tube. Its value, 15000 ohms, has been chosen to give sufficiently large but not excessively long pulses. With cables having an interconductor capacitance of up to 0.02 μf. this resistance results in pulses up to about one-third of a millisecond in length. For the present application it is considered unnecessary to reduce the pulse length by replacing part of the load resistance with inductance.

The trigger circuit (V5 and V6) is of the conventional type except that the biased tube is a pentagrid converter (V6). Grid No. 3 of this tube serves as the input grid for the neon audio-frequency oscillator (V7). During the conducting periods of V6, i.e., when a pulse trips the trigger circuit, the plate current of this tube is, therefore, modulated at the audio frequency (approximately 1000 c.p.s.). Two sets of coupling constants in the trigger circuit, selected by means of the "OFF-LO-HI" switch, give conducting periods of either 0.25 or 0.001 sec. approximately.

(d) Power Amplifier and Output Circuits

The resistance and capacitance in the coupling between the trigger circuit and the power amplifier (V8) are chosen to differentiate the (negative) pulses from the biased tube. The audio-frequency modulation on each pulse that arrives at the grid of the power amplifier has, therefore, a positive as well as a negative portion. The tube can then be biased to cutoff, thus making it convenient to operate the rate meter in the screen circuit and the speaker in the plate circuit of this tube. As normally used, i.e., with the range switch in the "LO" position, each "count" from the G-M tube thus gives a shrill note about 0.25 secs. long, in the speaker. The pitch of this note is such that it is not easily confused with other sounds in the vicinity, so does not keep the operators under a constant strain. The importance of this is realized when

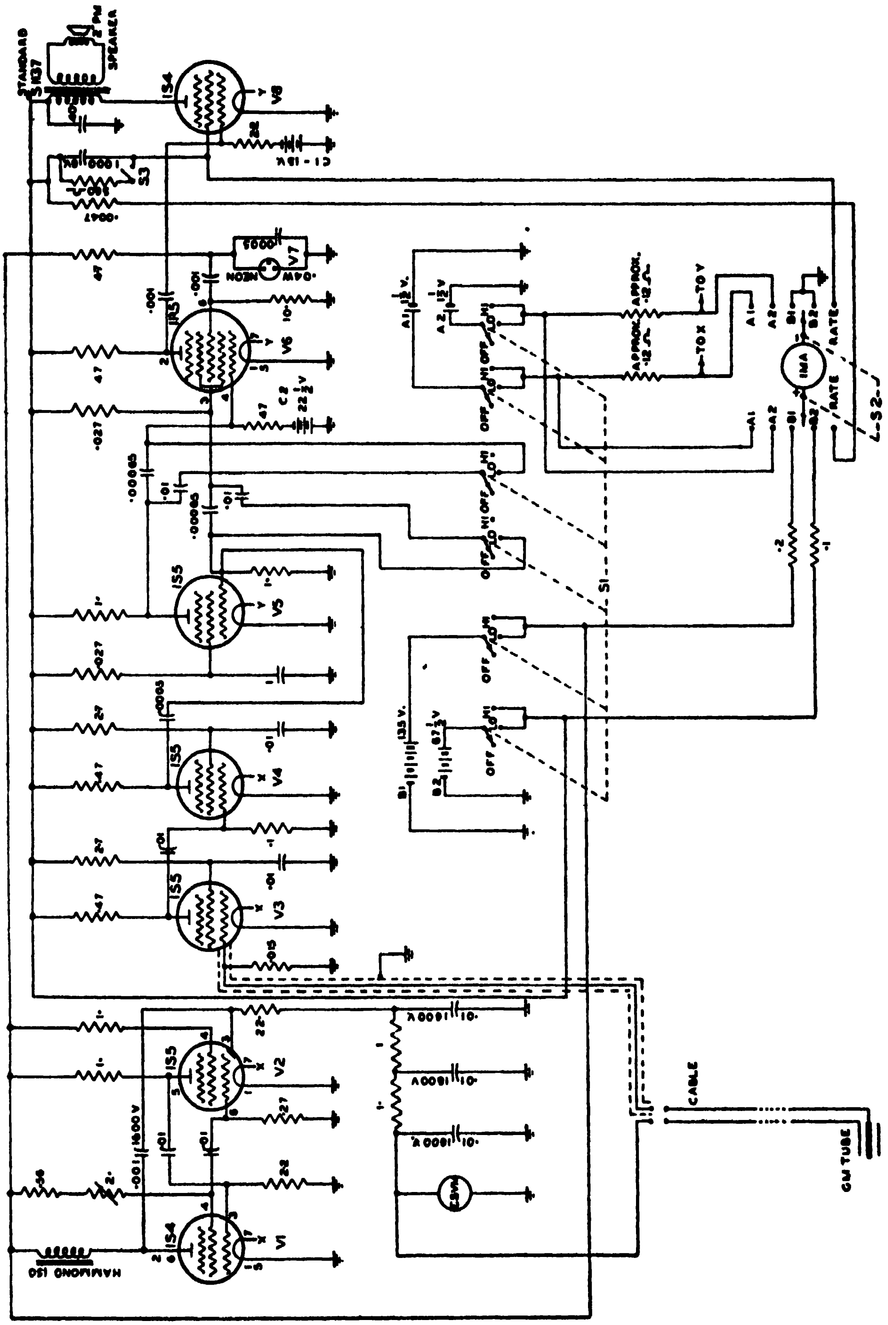

FIG. 1. *Circuit of a portable G-M counter for diamond drill holes. Resistances are given in megohms unless otherwise indicated, capacitances in microfarads.*

it is noted that during a large part of the time only the very low subsurface background activity is encountered. Under such conditions the lowering of the probe is halted to take rate meter readings only at 5 or 10 ft. intervals, yet narrow occurrences in between these points must not be missed.

The rate meter, which measures the averaged screen current in the power amplifier, has a time constant of about five seconds. A pushbutton switch S3 makes it possible to discharge the rate meter capacity quickly when desired. In the "LO" range the rate meter gives a full scale reading for about 200 counts per minute. In the "HI" range (pulse length approximately 0.001 sec.) it has a full scale sensitivity of about 2000 counts per minute. The modulated pulses from the trigger circuit are then too short for the audio tone in the speaker to be recognized as such. However, the higher counting rates that necessitate the use of this range partially compensate for this, and a satisfactory aural signal results. Also, under such conditions the more frequent rate meter readings taken render the aural signal less important.

The rate meter is essentially linear in each range. A decrease of 5 v. in the "B" voltage, however, results in a decrease in sensitivity of about 15%. For the present application this was not considered of sufficient importance to warrant the inclusion of means for setting the "B" voltage at a fixed value. Other factors influencing the sensitivity of the rate meter are discussed in Section *(f)*.

(e) Switching, Metering, Batteries, etc.

Two 1.5 v. "A" batteries (such as Eveready No. 742) have adequate capacity to permit continuous operation for several hours at a time. Two separate "B" supplies (made up of 67.5 v. batteries such as Eveready No. 467) are used to eliminate coupling between the input amplifier and the high voltage or neon oscillator circuits. One of these, B1, supplies 135 v. to permit the satisfactory operation of the neon oscillator. The bias supplies, C1 and C2, are provided by miniature batteries such as Eveready No. 411 (15 v.) and No. 412 (22 5 v.).

The switch *S2* allows the use of the 0–1 ma. meter, normally in the rate meter circuit, for checking the "A" and "B" batteries. It has been found very useful to include, also, an electrostatic voltmeter to constantly indicate the high voltage. The similarity between the low counting rates frequently encountered and the results in more active regions when the operating voltage is slightly too low is otherwise a constant source of worry. Also, problems connected with diagnosing trouble while the probe is hundreds of feet down a hole, or with setting the high voltage under operating conditions where the temperature in a hole is widely different from that at the surface, are greatly simplified.

(f) Selection of Components

Figures quoted above for the rate meter sensitivity, etc., are merely typical values. As may be expected, they vary considerably from unit to unit when commercial components with normal tolerances are used. Also variations in

characteristics of the individual electronic tubes have marked effects. The most important of these are discussed below:

(i) The use of a 135 v. "B" supply instead of the usual 67.5 v. (1) makes the selection of tubes for the high voltage circuit somewhat less critical than would otherwise be the case. However, the statements made in the above reference regarding the suitability of tubes for high voltage circuits still apply to a large extent.

(ii) It has been found that some 1R5 (V6) tubes used in the trigger circuit are not completely cut off by the 22.5 v. bias. In such cases a current of some 20 to 25 μa. flows through the tube. This does not seriously affect the operation of the trigger circuit. However, it does permit a signal from the neon circuit to be continuously passed. This causes a hum in the speaker and a spurious reading on the rate meter. If such tubes are excluded, variations in sensitivity of the rate meter with different 1R5's are slight. Somewhat greater variations in sensitivity, up to $\pm$ 10% are found with different 1S5's (V5).

(iii) The 1S4 in the power amplifier (V8) is sometimes not completely cut off by the 15 v. bias. This again gives rise to a spurious rate meter current, though in this case there is no associated speaker hum. Excessive bias on the other hand would cut down the sensitivity of the rate meter and the volume of the loudspeaker. In practice this spurious rate meter current seldom exceeds 0.05 ma. on the 1 ma. meter, but when such tubes are used the sensitivity of the rate meter may increase by as much as 20%.

Probes

The chief problem in constructing the probe is to make it waterproof under a 1000 ft. head of water. In the case of the glass walled G-M tubes, the tube is placed in a brass cylinder of 1⅛ in. external diameter. It was found unsatisfactory to use gland type seals at the point where the cable entered the brass cylinder, since under the necessary pressure the cable was deformed by the compressive gland. Probes filled with ceresin wax or with oil were found satisfactory, but are difficult to assemble under field conditions when replacement of the G-M tube becomes necessary.

All-metal, single ended G-M tubes coated with rubber promise to be more satisfactory. In making these probes a short length of cable is connected to the G-M tube. Rubber is then coated over the entire tube, connector, and a portion of the cable, to a diameter of 1 in. The end of the length of cable can be spliced to the main cable in the field without much difficulty.

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CANADIAN ERUCIC ACID OILS[1]

III. SHORTENINGS FROM RAPE AND MUSTARD SEED OILS

BY H. J. LIPS,[2] N. H. GRACE,[2] AND SUZANNE JEGARD[3]

Abstract

Processed rape and mustard seed oils were hydrogenated at 50 lb. pressure and 284° F., using a commercial nickel formate catalyst, and were deodorized for one hour at 464° F. The stability of the hardened oils compared favorably with that of a standard commercial vegetable shortening. Taste panel tests indicated that both the rape and mustard shortenings were as satisfactory as the commercial reference material for the preparation of pastry and doughnuts. Special study of the rape product showed that it could be plasticized, and it gave good results in baking volume experiments.

Introduction

In the nonselective hydrogenation of vegetable oils commonly employed in the manufacture of shortening, some (combined) stearic acid is formed by complete saturation of oleic acid, and some elaidic acid by geometrical transformation of oleic acid (2, p. 565). The comparable reactions in erucic acid oils would lead to the formation of behenic and brassidic acids from erucic acid. In view of the widely different melting points and structures of the possible fatty acid products, it might be expected that shortenings from erucic acid oils could differ markedly from those in ordinary use. Moreover, Canadian shortening manufacturers have suggested verbally that hardened erucic acid oils may be inferior in baking volume properties. On the other hand, Canadian rape and mustard seed oils were shown to possess potential value as salad and cooking materials (6), and hardened rape seed oil was eaten during the war in Germany (4), so it might be expected that shortenings from rape and mustard seed oils would be acceptable food products. Estimation of possible consumer reaction to shortenings prepared from these oils by a standard method was therefore undertaken, with special consideration to the effect of rape shortening (the more important product) upon baking volume.

Materials and Methods

The processing of the crude rape and mustard seed oils used in this work has been described (3, 6). In brief, they were refined with 10° Bé. alkali and bleached under nitrogen with 2% Superfiltrol for 20 min. at 212° F.

The oils were then hydrogenated in a pilot-scale, stainless steel hydrogenator of 10 lb. capacity, at 50 lb. pressure and 284° F., with purging at 15 min. intervals. The catalyst was commercial nickel formate (25% nickel) at

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[2] *Biochemist, Oils and Fats Laboratory.*

[3] *Biochemist, Food Investigations.*

1% concentration. The course of hardening was followed by withdrawing samples and determining the refractive index. When the desired hardness was reached, the material was removed from the hydrogenator, 1% diatomaceous earth was added, and the mixture was filtered in a porcelain Büchner funnel. The shortening was then steam deodorized under vacuum in an all-glass apparatus for one hour at 464° F. Each test shortening was a composite of two or three individual preparations. A standard commercial vegetable shortening of high quality was used as reference material in all tests, and comparisons were made both with fresh shortenings and shortenings aged for 10 days at 100° F.

Color, fluorescence, kinematic viscosity, peroxide oxygen, free fatty acid, and smoke point were measured at different stages of use of these materials, as previously described (3, 6). Iodine value was determined by a modification of Wij's method (5) and melting point by the capillary tube method (1).

Pastry and doughnuts were prepared with the shortenings according to the recipes given in Table I. Pastry was baked 10 min. at 435° F. and served at

TABLE I

RECIPES FOR DOUGHNUTS AND PASTRY, GIVEN IN GRAMS

Constituent	Doughnuts	Pastry
Eggs	96	—
Flour	500	112
Sugar	200	—
Shortening	25	66
Milk	224	—
Water	—	30
Baking powder	15	—
Cinnamon	½	—
Nutmeg	½	—
Salt	4	2

room temperature; doughnuts were fried in the shortenings at 355° to 365° F. for three minutes and served warm. Pastry and doughnuts were scored for taste and odor by a 24-member panel as previously described (6); excess or deficiency of the property was rated on an integral scale of + 5 to − 5.

After some preliminary trials, the following biscuit volume method (Method *A*) was developed to determine the effect of shortenings on baking volume: 100 gm. of flour, 3.5 gm. of baking powder, and 1.3 gm. of salt were mixed for one minute in a jacketed dough mixer held at 100° F. Fat (17 gm.) warmed to a temperature of 140° F. was added to the dry mixture and the mixing process continued for another minute, then 50 ml. of water was added and mixed in for one minute more. The total mixing time was three minutes. A 100 gm. sample of this batter was weighed into a small baking tin and baked for 30 min. at 475° F. The volume of the baked biscuit was measured

by a rapeseed displacement method (7). In variations of this procedure, 60 ml. of water was used instead of 50 ml. (Method *B*); and unmelted rather than melted fat was used (Method *C*).

Results

Shortening Measurements

Tables II and III present physical and chemical measurements for the commercial, mustard, and rape shortenings. The commercial shortening had a lower iodine value and melting point (Table II) than the rape and mustard

TABLE II

CHARACTERISTICS OF SHORTENINGS USED FOR TASTE PANEL TESTS

Shortening	Melting point, ° C.	Iodine value
Commercial	38.0	57.9
Mustard	42.9	67.6
Rape	45.4	58 3

shortenings of about the same hardness chosen for comparative test. The relative transmissions at 440 and 660 mμ of the rape and mustard products were similar, and slightly less than those of the commercial material (Table III). Indications were (Table III, *C*) that the color was not sufficiently intense to interfere with the measurement of fluorescence. Fluorescence in ultraviolet light (375 mμ) increased in the order: rape, commercial, mustard; and viscosity in the order: commercial, mustard, rape. Peroxide and free fatty acid values were uniformly low. The commercial shortening had the highest smoke point, with rape shortening next, and mustard shortening lowest but still fairly satisfactory.

These characteristics were altered in varying degree by aging the shortenings or by using them for the deep fat frying of doughnuts (Table III): transmission was not changed by aging but decreased markedly with frying; fluorescence increased with frying; viscosity was practically constant;

TABLE III

CHEMICAL AND PHYSICAL MEASUREMENTS ON SHORTENINGS AT VARIOUS STAGES OF USE

Shortening	Condition of shortening			
	Fresh	Aged	Fresh, fried	Aged, fried
	Measurement			
	A. Transmission, per cent at 440 mμ and 60° C., relative to mineral oil (Stanolax)			
Commercial	68	68	48	56
Mustard	58	55	38	36
Rape	61	61	48	35

TABLE III—*Concluded*

CHEMICAL AND PHYSICAL MEASUREMENTS ON SHORTENINGS AT VARIOUS STAGES OF USE—*Concluded*

Shortening	Condition of shortening			
	Fresh	Aged	Fresh, fried	Aged, fried
	Measurement			
	B. As in A, at 660 mμ			
Commercial	98	97	95	97
Mustard	92	92	96	96
Rape	90	91	95	94
	C. Transmission, per cent at 440 mμ of 1 gm. of shortening in 100 ml. xylol, relative to xylol			
Commercial	99	100	99	100
Mustard	99	99	99	99
Rape	100	99	99	98
	D. Fluorescence, Coleman photofluorometer units, 1 gm. of oil in 100 ml. xylol, corrected for fluorescence of xylol			
Commercial	16	13	18	18
Mustard	32	33	38	38
Rape	12	10	19	17
	E. Viscosity, centistokes at 130° F			
Commercial	27 2	27 6	27 2	27 5
Mustard	30 6	30 4	30 2	30 2
Rape	33 3	33 8	34 0	33 8
	F. Peroxide value, ml of 0 002 N thiosulphate per gm.			
Commercial	0 0	0 0	2 8	4 9
Mustard	0 0	0 0	4 3	3 9
Rape	0 0	0 0	3 8	3 7
	G. Free fatty acid content, as % oleic acid			
Commercial	—	—	0 1	0 1
Mustard	—	—	0 2	0 2
Rape	—	—	0 2	0 2
	H. Smoke point, ° F.			
Commercial	430	427	398	399
Mustard	387	385	385	372
Rape	414	410	388	382

peroxides were detectable only in the fried shortenings; smoke points were lowered slightly by aging, and to a greater extent by frying.

Taste Panel Tests

Taste panel ratings for all pastry and doughnut products (Table IV) showed no difference between doughnuts prepared from any of the types of shortening tested but, on the average, odor and flavor of pastry made with the experimental fats were rated as slightly preferable to those of pastry made with similar amounts of the commercial shortening.

TABLE IV

AVERAGE PANEL SCORES FOR ODOR AND FLAVOR OF PASTRY AND DOUGHNUTS *

Shortenings	Pastry		Doughnuts	
	Odor	Flavor	Odor	Flavor
Fresh:				
Commercial	+ 0 5	+ 0 4	+ 0 1	+ 0 1
Mustard	+ 0 1	+ 0 1	+ 0 2	+ 0 1
Rape	+ 0 2	+ 0 2	+ 0 1	+ 0 2
Aged:				
Commercial	+ 0 5	+ 0 7	+ 0 2	+ 0 2
Mustard	+ 0 1	+ 0 2	+ 0 2	+ 0 2
Rape	+ 0 1	+ 0 2	+ 0 2	+ 0 2
Necessary difference (5% level of statistical significance)	± 0 4	± 0 4	± 0 3	± 0 4

Baking Volume

Different samples of hydrogenated rapeseed oil, with iodine values from 40 to 100, showed no significant volume difference by baking methods *A* or *B* in two series of hydrogenated oils (Table V). The additional water added in Method *B* caused a general increase in baking volume that was significant for most of the shortenings tested. However, when unmelted fat was used (Method *C*), the rapeseed biscuits were significantly smaller than the reference biscuits if the hydrogenated oil had an iodine number less than about 85. Biscuits made from the commercial product had the same baking volume regardless of the state of the fat. These results indicated that when the unmelted rapeseed shortening was used some physical factor interfered with fat distribution in the mixture and resulted in an inferior baking volume.

The hydrogenated rapeseed oil was then plasticized to make its consistency approximate more closely that of the standard commercial shortening. The steps in the plasticizing process were: (*a*) preliminary heating of the fat to 212° F., (*b*) beating of the melted fat in a Mixmaster with rapid cooling at −40° F. until the mass solidified, and (*c*) tempering the plasticized product at 80° F. for three days. Two samples of plasticized fat were prepared from

TABLE V

COMPARATIVE BISCUIT VOLUMES FOR HYDROGENATED RAPESEED OILS AND A COMMERCIAL VEGETABLE SHORTENING

(Averages of three determinations)

Description of samples			Biscuit volume, ml.		
Shortening	Iodine No.	M.p., °C.	Method *A* (50 ml. water)	Method *B* (60 ml. water)	Method *C* (unmelted fat)
Standard (commercial vegetable shortening)	57.9	38.0	195	210	195
Hardened rapeseed oils, samples taken at intervals during hydrogenation:					
Hydrogenation series I	103.2	< 15.0	204	208	—
	90.0	18.0	199	212	—
	65.9	42.0	200	214	—
	49.2	49.8	196	—	—
	44.5	52.0	199	210	—
Hydrogenation series II	100.5	< 15.0	198	—	194
	87.8	23.3	202	—	186
	63.8	42.8	197	—	183
	55.0	47.6	197	—	184
Necessary difference (5% level of statistical significance)				10	

a rapeseed shortening of melting point 46° C., which was higher than the melting point of the commercial shortening (38° C.). The plasticized products were found to have good mixing properties in the solid form. Biscuits were baked with the fat in an unmelted state. The resulting volumes were:

Unplasticized — 184 ml.

Plasticized sample No. 1 — 191 ml.

Plasticized sample No. 2 — 196 ml. (a significantly higher figure than for the same material unplasticized)

Commercial — 195 ml.

These figures showed that the hydrogenated rapeseed oil could be plasticized to give as good a biscuit volume as the standard commercial vegetable shortening.

Conclusions

Hardened erucic acid oils prepared by a standard method did not differ markedly from ordinary shortening in the properties studied, in spite of inherent compositional differences. No special hardening techniques were necessary to prepare shortenings acceptable as food products from processed

Canadian rape and mustard seed oils. These shortenings were stable materials of fair color and smoke point, and were amenable to plasticization and use in baking.

Acknowledgments

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LABORATORY STUDY OF LOW RATIO BUTADIENE-STYRENE COPOLYMERS[1]

By J. M. Mitchell[2] and H. Leverne Williams[3]

Abstract

The copolymerization of styrene and butadiene in ratios in which the styrene equals or predominates over the butadiene on a mass basis is essentially similar to copolymerization in the presence of a predominance of butadiene. However, the rate of reaction and the length of the induction period is increased. Increasing the amount of the dodecyl mercaptan regulator results in a slight increase in rate and diminution of the induction period. The dodecyl mercaptan reacts at a lower rate than during the production of GR-S. The regulating index as defined by the ratio of the logarithm of the residual mercaptan over the conversion is 1.53. The bound styrene and increment styrene curves seem to be normal and indicate reactivity ratios r_1 (butadiene) equal to 1.4 to 2.2, r_2 equal to 0.5 to 0.7. If these reactivity ratios are corrected for the bifunctional nature of butadiene then the constants for butadiene monomer are Q equal to 0 9 and e equal to -1. Likewise the gel-viscosity data are similar to those observed with GR-S except that the pre-gel rise in viscosity, the formation of gel, and the slope of the viscosity conversion curves diminish with increasing styrene in the charge. The chain transfer action of styrene is increasingly evident with increasing styrene content in the charge but in all cases the regulating effect of dodecyl mercaptan is still apparent.

Introduction

Butadiene and styrene may be copolymerized in all proportions and the resulting copolymers vary in their characteristics between the properties of pure polybutadiene and pure polystyrene but not necessarily like a mechanical mixture of the two pure polymers in the same proportions. An earlier investigation (20, 21) described the effect of the change of butadiene-to-styrene ratio from 90/10 to 50/50 on the physical properties of rubber vulcanizates. Preliminary to a similar study in the lower butadiene to styrene ratios, it was essential to obtain certain small scale laboratory data similar to those described in numerous publications for chemical rubber. Only scattered data of this type are available. Meehan (23) has studied the composition of copolymers over both ranges. Fragmentary data are in the various papers on the use of the copolymers (1, 5, 6, 7, 9, 11, 15, 19, 26, 27, 31, 32) as fillers, reinforcers, resins, or rubbers.

Techniques

All reactions were conducted in 8-oz. screw cap bottles fitted with a gasket (12) for syringe sampling (14). The soap solutions, styrene, and regulator and, for the 15/85 ratio copolymers, the initiator were weighed into the bottle and a slight excess of butadiene added. The excess butadiene was allowed to vaporize to drive out the air in the bottle, which was capped when it had reached the correct weight. The bottles were then placed in the constant

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[2] *Junior Chemist.*
[3] *Research Chemist.*

temperature bath and rotated end over end for 30 min. until they had reached the desired temperature. At that time, usually, the initiator solution was injected by syringe and needle and the agitation resumed. The initiator was added before capping the 15/85 charges since these soon developed, inside, a low pressure which tended to suck water through the punctured self-sealing gasket. Nitrogen pressure was used to facilitate sampling at the end of the reaction. After the appropriate time a sample was removed by syringe and needle and a known weight of latex dried to determine the conversion of hydrocarbon to resin. Just before the reaction was stopped, a 10 ml. syringe sample of the latex was obtained, on which a duplicate determination of unreacted mercaptan was done by amperometric titration (16) with 0.005 N silver nitrate.

When the reaction was to be terminated, the solution of hydroquinone was injected into the bottle, which was then shaken vigorously and allowed to cool. After the reaction was stopped, the final conversion of hydrocarbon to resin was determined on each sample using the unvented solids technique. Excess butadiene was vented by insertion of a needle through the gasket and finally excess monomers were removed by steam distillation.

Recovery of the polymer was effected by coagulating one-half of the latex with sodium chloride – sulphuric acid mixture, washing the coagulum, and drying. If the polymer were to be preserved then sufficient BLE dispersion was added before coagulation to give 1.5% BLE based upon the dry resin.

Dilute solution viscosities were measured as reported earlier (8), i.e., by the four-point method using a modified Ubbelohde pipette and benzene as solvent. Corrections for nonrubber solids in the dry polymer are shown in Table I and are applicable to all polymers prepared in the recipe shown in

TABLE I

PER CENT RESIN IN DRY PRODUCT AT VARIOUS CONVERSIONS

Conversion, %	Total solids based on 100 parts monomer charge, %	Resin in dry product corrected for 1.5 parts BLE, %
0	6 11	0
1	7 11	13.9
2	8 11	24.3
3	9 11	32.4
5	11.11	44.4
10	16.11	61.2
15	21 11	70 0
20	26.11	75.5
30	36.11	81.9
40	46.11	85.5
50	56 11	87.8
60	66.11	89.5
80	86.11	91.5
100	106.11	92 9

Table III regardless of the charge ratio. The amount of gel (benzene insoluble) was the difference between the mass of polymer placed in benzene and the amount that dissolved. The swelling index was the ratio of the weight of swollen gel and imbibed solvent to the weight of dry gel.

The remaining unstabilized latex was coagulated with isopropanol and given three successive, five minute washes in fresh alcohol to remove all alcohol soluble materials. The polymer was dried at 100° C. in a vacuum oven for three hours, sheeted on a tight mill, and its refractive index measured at 60° C., using an Abbé refractometer through which water at 60° C. was circulated. The bound styrene of those polymers prepared with 70 to 85 parts of styrene in the charge was read from a graph relating it to the refractive index at 60° C. A straight line relation between GR-S chemical rubber and polystyrene was assumed; and a check on the values was obtained by using a soft polymer and the familiar refractive index technique at 25° C. involving the equation

$$\text{Bound styrene} = 22.94 + 1180\,(n_D^{25} - 1.5339) - 2340\,(n_D^{25} - 1.5339)^2.$$

The cross check data are shown in Table II and indicate that the answers agree very well. The results measured at 60° C. may be 1 to 2% higher than those measured at 25° C. The bound styrene of the 50/50 ratio copolymers was measured at 25° C.

TABLE II

CROSSCHECK DATA ON REFRACTIVE INDICES

Sample No.	n_D^{60}	Styrene in resin, %	n_D^{25}	Styrene in resin, %
1	1.5527	58.0	1.5650	57.4
2	1.5531	58.4	1.5654	57.7
3	1.5559	61.9	1.5690	61.4
4	1.5586	64.6	1.5712	63.7
5	1.5616	68.4	1.5743	66.8

Experimental

The basic charge formula resembled those in general use and is shown in Table III. It was very similar to that used in the preparation of Rubber Reserve polymer X-323. At 50° C. as used for GR–S chemical rubber the reaction was too rapid, especially when the 20/80 and 10/90 butadiene–styrene ratios were used. To obtain adequate results the samples were prepared at 45° C. A preliminary survey of the field yielded the data in Table IV. In all cases 0.15 part of dodecyl mercaptan was used, based upon the monomers.

These data indicated that no serious difficulty was to be expected and it was decided to investigate three monomer ratios in greater detail. The effect of charge ratio of butadiene to styrene and amount of dodecyl mercaptan charged upon rate is shown in Fig. 1. It is evident that as the amount of

TABLE III

FORMULA FOR POLYMERIZATION SYSTEM

Butadiene (commercial pure)	Variable	Total 50 gm.
Styrene (commercial pure)	Variable	
Dodecyl mercaptan	Variable	
S.F. soap flakes, gm.	2 25	
Daxad 11,* gm.	0 50	
Potassium persulphate, gm.	0.15	(6 ml. of 2 50% sol'n.)
Distilled water, gm.	112 50	
Stopping agent hydroquinone, gm.	0 08	(2 ml. of 4% sol'n.)
Antioxidant BLE*, %	1 5	Based upon dry resin

Trade names, no simple chemical formula.

TABLE IV

COPOLYMERIZATION OF STYRENE AND BUTADIENE IN VARIOUS RATIOS

Butadiene to styrene charge ratio, parts	Reaction time, hr.	Conv. %	Gel, %	Swelling index	[η]
50/50	4¼	18 5	1	—	2.06
"	8	55 5	9	36	2.42
"	12	64 2	65	60	2.44
"	16	78 8	74	70	1 05
40/60	4¼	21 5	10	52	2 45
"	8	58 5	4	26	3.04
"	12	71 3	71	82	1 58
"	16	-	—	—	—
30/70	4	21 6	4	--	1 25
"	8	55 3	6	—	1 36
"	13⅔	85 3	73	53	2 28
20/80	2½	9 1	—	—	—
"	5⅙	38 6	—	—	—
"	7½	58 5	—	—	—
"	12	89 5	—	—	—
10/90	2½	6 9	—	—	—
"	5⅙	34 0	—	—	—
"	7½	73 7	—	—	—
"	12	93 5	—	—	—

butadiene in the charge is diminished there was an increase in the rate of conversion to resin. At 45° C. the rate was about twice as great with 15/85 ratio as with the 50/50. Also it can be seen, particularly in the case of the 50/50 ratio that the increasing amount of mercaptan resulted in a greater yield in a given time by shortening the initial induction period. It is evident, too, that increasing the styrene in the charge had lengthened the induction period slightly. This could be due to either the increased difficulty of purging the bottles of air or to the increased inhibitor added with the styrene. The conversion of monomers to GR–S at 50° C. would be very similar to the lower broken curve of Fig. 1.

The rate of disappearance of dodecyl mercaptan was insensitive to charge ratio of butadiene to styrene and to the amount of mercaptan charged within

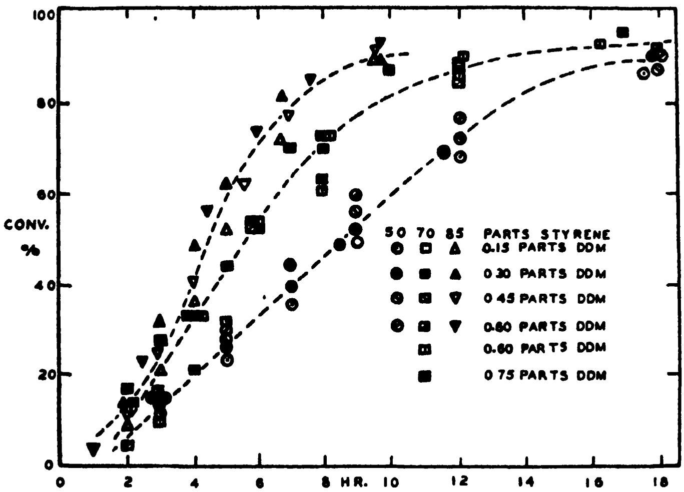

FIG. 1. *Time-conversion curves for various ratios of butadiene to styrene and with various amounts of dodecyl mercaptan at 45° C. Broken lines represent average curve. Time-conversion curve for GR-S at 50° C. is almost identical with the lower broken curve.*

the limits studied, as shown in Fig. 2. The data when an average curve was estimated indicated slight or negligible consumption of mercaptan during the first few per cent conversion of hydrocarbon to resin when 70, and particularly 85, parts of styrene were charged. A representative curve for GR-S is shown and can be seen to lie below all the experimental data of this series.

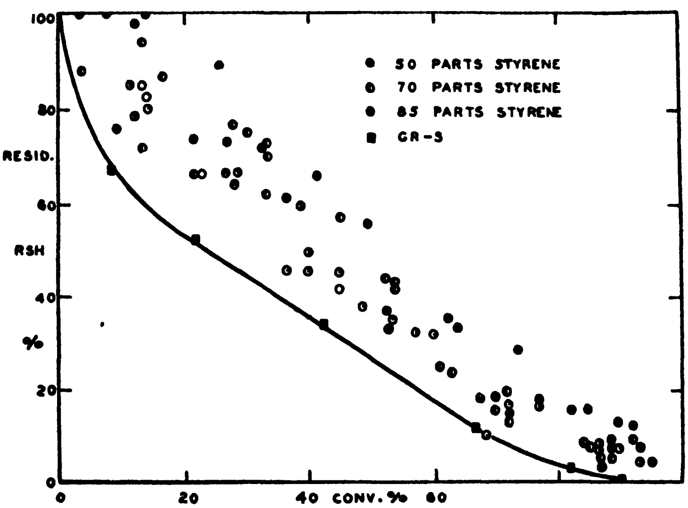

FIG. 2. *Residual mercaptan for various charge ratios of butadiene to styrene and all amounts of dodecyl mercaptan charged as a function of conversion at 45° C. Lower curve is a typical result for GR-S at 50° C.*

If the data were plotted in the form *ln* (% residual mercaptan) versus per cent conversion the initial slope of the straight line portion became by definition the regulating index. For all three charge ratios and all mercaptan charges this was found to be 1.53. Since the straight line portion extrapolates to 100% or higher there is no waste factor. The comparable figures for GR–S were 2.39 and 19% respectively from the curve of Fig. 2.

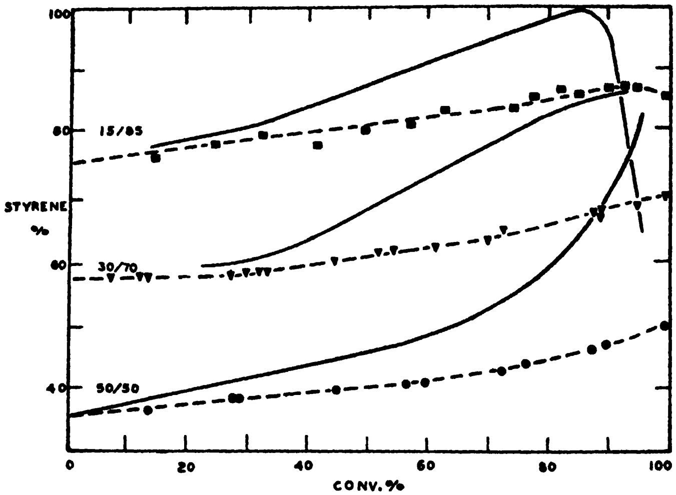

FIG. 3. *Bound styrene (broken lines) and increment styrene (solid lines) for various charge ratios of butadiene to styrene as a function of conversion at 45° C.*

The bound styrene, Fig. 3, followed the same general form (20, 21, 23) as those published previously. The data for the 30/70 butadiene-to-styrene ratio indicated a leveling off of the increment styrene at higher conversions. This was accentuated and the increment styrene curve reversed for the 15/85 ratio. The explanation might be that the refractometric method of measuring the bound styrene at 60° C. was, indeed, indicating values about 2% high. A more precise measure of bound styrene over this range would be necessary to clarify the cause.

From the general copolymerization equation (2, 3, 22, 28)

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}$$

and assuming an ideal case, i.e.,

$$\frac{d[M_1]}{d[M_2]} = \alpha \frac{[M_1]}{[M_2} = \alpha R,$$

the values of R and α have been calculated for the three ratios from the bound styrene data obtained by extrapolating to zero conversion. The data are in Table V.

TABLE V

REACTIVITY RATIO CALCULATIONS

Butadiene-to-styrene charge ratio	$d[M_2]$ Styrene at 0 conv., %	$d[M_1]$ Butadiene at 0 conv., %	$\frac{d[M_1]}{d[M_2]}$	R	α
50/50	34.8	65.2	1.872	1.00	1.87
30/70	57.8	42.2	0.729	0.429	1.70
15/85	75.6	24.4	0.323	0.177	1.82

Using the values of R and α the values of r_1 and r_2 were calculated from the equation

$$r_1 = \frac{\alpha}{R} r_2 + \left(\alpha - \frac{1}{R}\right),$$

and plotted as in Fig. 4. From the dimensions of the resultant triangle the value of r_1, the ratio of the reactivity of butadiene radical with butadiene over its reactivity with styrene, ranged from 1.4 to 2.2, whereas r_2, the ratio of the reactivity of the styrene radical with styrene over the reactivity with butadiene, lay between 0.5 and 0.7.

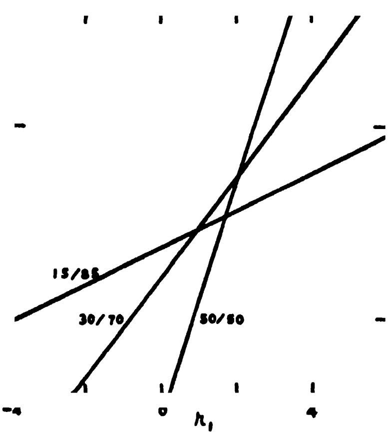

FIG. 4. *Plot of r_1 versus r_2 to obtain the range of the probable values of the reactivity ratios.*

These reactivity ratios were calculated on a molar basis without regard for the two double bonds present in butadiene. Assuming that each of these double bonds possessed the same reactivity, the reactivity ratios may be corrected for the two double bonds, that is, converted to a "double bond" rather than molar basis. When this is done the characteristic constants Q and e (4) may be calculated (4, 10). These were 0.9 and -1 for butadiene. Q may be considered the mean reactivity of the butadiene double bond and e may be considered proportional to the charge on the butadiene radical and group relative to Q and e for styrene of 1 and -1 respectively.

The gel and viscosity data for the 50/50 ratio copolymers are shown in Fig. 5. It was apparent that, as polymerization proceeded, the dilute solution viscosity of the polymer rose slowly. Then at fairly high conversions cross

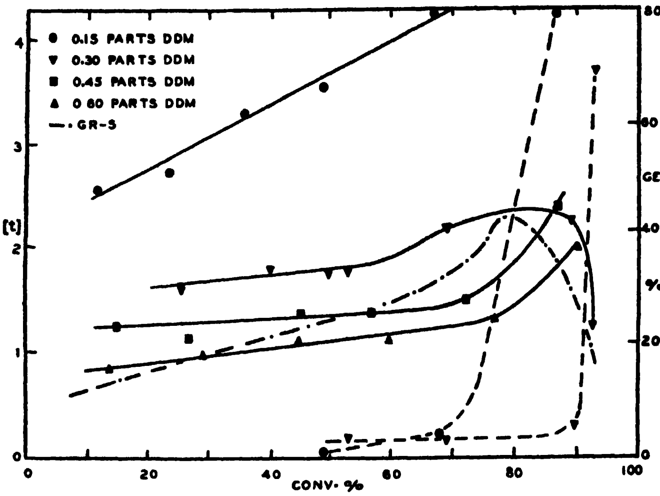

FIG. 5. *Dilute solution viscosity (solid line) and gel (broken line) data for 50/50 butadiene to styrene copolymers with various amounts of dodecyl mercaptan in the charge as a function of conversion at 45° C. Curve (—·) is a typical one for GR-S at 50° C.*

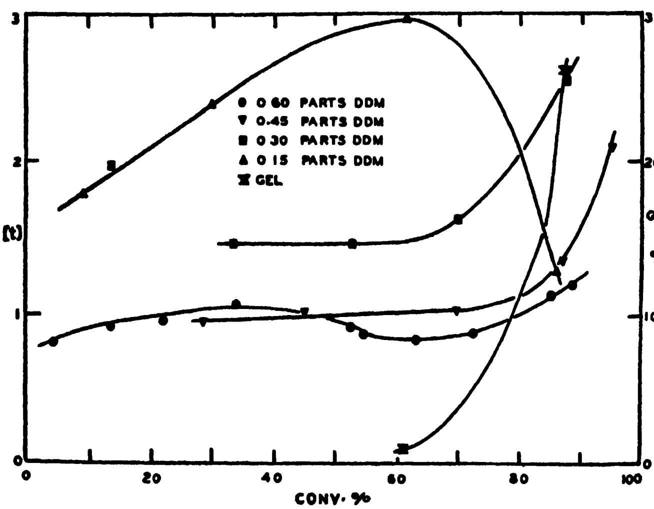

FIG. 6. *Dilute solution viscosity and gel (0.15 parts DDM only) data for 30/70 butadiene-to-styrene copolymers with various amounts of dodecyl mercaptan in the charge as a function of conversion at 45° C.*

linking and branching started, at which time the viscosity rose rapidly, then fell sharply when gel formed and was removed, leaving only low molecular weight material. It is evident also that, as the amount of dodecyl mercaptan regulator added was increased, the viscosity, i.e., molecular weight, of the

copolymer was diminished and the rise in the viscosity with conversion was less marked and more delayed. These same observations were noted with the 30/70 ratio copolymers, Fig. 6. In this case the polymers prepared using 0.60 part of dodecyl mercaptan seemed to be out of line. However, no irregularity was noted with the 15/85 ratio, Fig. 7. In this the viscosity of the

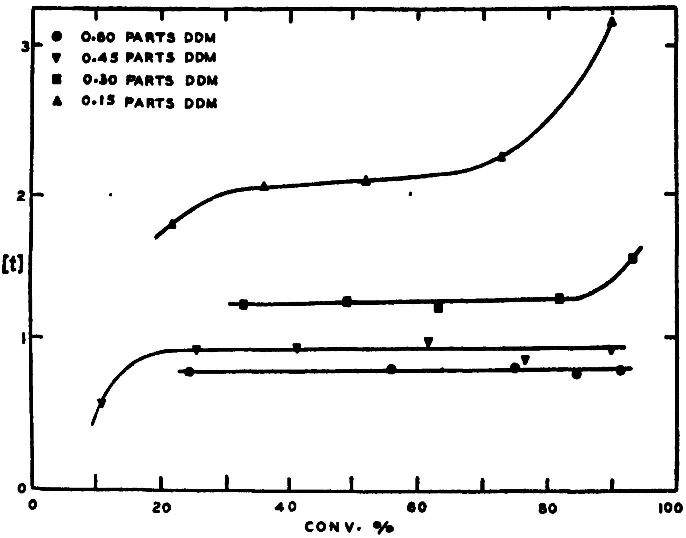

FIG. 7. *Dilute solution viscosity data for 15/85 butadiene-to-styrene copolymers with various amounts of dodecyl mercaptan in the charge as a function of conversion at 45° C.*

polymer remained remarkably constant up to quite high conversions before there was the increase in viscosity with conversion. Comparison of Figs. 5, 6, and 7 will show that under comparable conditions the increase in styrene in the charge resulted in a lower viscosity polymer by increased chain transfer due to the styrene, and the formation of higher molecular weight material including gel is delayed. Additional data over a narrow range of concentrations and pertaining to the 30/70 ratio in the proximity of the normal commercial conversion range are in Table VI. The reaction time was 10.5 hr. at 45° C.

TABLE VI

MERCAPTAN-VISCOSITY RELATION

Resin	Conversion, %	Gel, %	[t]	Parts dodecyl mercaptan
1	77.7	4	1.30	0.45
2	78.2	1	1.43	0.35
3	77.9	3	1.47	0.30
4	78.0	1	1.98	0.25
5	77.0	6	2.83	0.15

The effect of the butadiene-to-styrene ratio in the charge is likewise amply demonstrated by the data in Table VII, which shows a comparison of three copolymers of general commercial use. With increasing styrene in the charge the rate of the reaction was increased and the amount of dodecyl mercaptan required for approximately the same dilute solution viscosity and solubility was reduced.

TABLE VII

DODECYL MERCAPTAN REQUIREMENTS FOR COPOLYMERS OF COMPARABLE VISCOSITY

	Butadiene to styrene ratio		
	70/30	50/50	30/70
Parts dodecyl mercaptan	0.425	0.320	0.214
Reaction time, hr.	13	8⅔	5½
Solids, %	27.4	23.8	23.0
Conversion, %	74.3	74.0	70.3
Soluble in benzene, %	96	95	89
Gel, %	4	5	11
[*t*]	1.92	2.16	2.20

Although in all cases the corrected dilute solution viscosity was measured using dry polymer, it was of interest to try the modified vistex viscosity technique whereby latex is dissolved in mixed solvents, benzene/isopropanol 80/20, and diluted by successive portions of benzene in the usual manner. Plotting the data allows extrapolation to zero nonsolvent (20, 25). The data in Table VIII indicated that while the preliminary agreement was not perfect the method has sufficient promise to warrant regular usage. The vistex tech-

TABLE VIII

INTRINSIC FLOW TIME BY VISTEX AND DILUTE SOLUTION TECHNIQUES IN BENZENE

Sample No.	[*t*], vistex	[*t*], dilute solution
SM-31-2	0.85	0.85
3	0.84	0.78
4	0.75	0.74
5	0.78	0.72
6	0.81	0.74
SM-33-3	1.85	1.44
4	1.22	1.33
5	1.32	1.31
6	1.55	1.69
SM-34-2	2.22	2.28
3	2.38	2.39
4	2.22	2.34
5	2.36	2.46
6	3.20	3.42
SM-30-3	3.01	3.24
4	3.25	3.50

nique seemed to yield high results for low viscosity polymers and low results for high viscosity polymers relative to the usual dilute solution technique.

Discussion

The system, generally, behaves very similarly to that used for the production of GR–S chemical rubber. The only change in the recipe is the addition of a stabilizing agent, Daxad 11, since during the polymerization the latex particles tend to adhere together or agglomerate, forming prefloc or precoagulum. In this respect the latex has been observed to be quite unstable without this precaution. The rate of the reaction is greater, as can be noted by comparison of the data in Table VII, or Fig. 1, or with similar data obtained at 50° C. (17).

The effect of mercaptan of increasing the rate is well known in the preparation of GR–S (25). Comparison of the regulating index reveals that this is lower for dodecyl mercaptan in the higher styrene ratios than it is for GR–S type copolymers (18, 24). There does not appear to be a waste factor, indeed just the opposite. It is suggested that the increased rate of reaction makes the rate of diffusion of the mercaptan play an increasingly important role until the so-called phase inversion takes place at about 60% conversion. At such a time diffusion no longer is taking place, and particularly with the higher dodecyl mercaptan charges there is an increased rate of disappearance and, in the case of the 30/70 ratio copolymer, a decrease in the viscosity of the polymer found.

The viscosity, unlike that for GR-S (29, 30), does not tend to rise as rapidly, there is less tendency for the pre-gel sharp rise, and when using higher styrene charges and dodecyl mercaptan charges there is indeed no indication of either a rising viscosity or of gel formation up to over 90% conversion. This must be associated with the lower unsaturation of the resin.

The bound styrene data and the values derived from it are more uniform and suggest a system more nearly ideal than that found by Meehan (23). Perhaps the large number of experimental points explains this. In general the data agree well. All suggest that measurements of bound styrene at 60° C. are about 2% absolute high, and allowing for this error the increment styrene curves would be normal. The values for the reactivity ratios are slightly higher than those reported by Meehan (23). No correction was made for bound mercaptan but available data suggest that only a small correction need be made for this.

The calculations of the reactivity ratio in the normal manner yield results that neglect the bifunctional character of butadiene. The correction for this, that is, of assuming each double bond equally reactive, would seem logical at least as a first approximation. The derived values of Q and e agree with experience. The vinyl substituent group is considered to activate the vinyl group as much as, if not more than, does the phenyl group; that is, butadiene double bonds are as reactive as styrene double bonds. On the other hand, the

free radical formed of a butadiene end group is about as active as a styrene one; the growth of a copolymer chain seems to be entirely random.

Acknowledgments

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The technical assistance of A. Johnston and G. Vincent is gratefully acknowledged.

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A DYNAMOMETER FOR DETERMINING DEPTH OF FREEZING IN FOODS[1]

By H. Tessier[2]

Abstract

A dynamometer, designed to determine depth of freezing in frozen foods, such as meat, poultry, and eggs, measures the force required to drive a pointed rod through a sample of the product.

Introduction

The depth of the frozen portion of some food products is frequently a matter of controversy that is often settled by breaking open some units of the frozen food with an ax, thus destroying those units. Often, the depth of freezing is determined by driving a nail into the product. Lack of resistance to the nail indicates an unfrozen portion. This paper describes a dynamometer that will give a semiquantitative estimate of the depth of freezing in foods.

Description

The dynamometer (Fig. 1) consists of a brass cylinder (*A*) at the lower end of which a chuck (*B*) holds a removable pointed rod (*C*). The upper part of the cylinder is threaded to receive a screw cap (*D*) which clamps down the ringhead (*E*) of a bellows (*F*) against a rubber seal (*G*). A steel rod (*H*) screwed into the lower part of the bellows (*I*) guides a metal ram (*J*). The ram weighs 1 lb. and slides freely over the guide. When this ram is brought down with muscular force against an anvil (*K*), the oil that fills the space between the bellows and the cylinder permits the pressure exerted by the blow to be indicated on a pressure gauge (*L*) connected to the cylinder through a bushing (*M*). To prevent damage to the bellows, a stop (*N*), soldered to a screw cap (*D*) limits the upward movement of the bellows when the ram is pulled up against a nut (*O*) or when the point is pulled out of the sample. For convenience when the instrument is not in use, the guide rod can be unscrewed from the anvil and the pointed rod can also be removed from the chuck.

Procedure

The pointed rod is held against the frozen sample, the ram is gripped firmly with one hand and brought down with force against the anvil until the point penetrates the sample. The pressure at each stroke is noted on the gauge. In a completely frozen sample the pressure required to drive the point into the center of the sample is approximately the same for every stroke, but the

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[2] *Technical Officer, Food Investigations*

pressure required and the depth of penetration at each stroke varies with the temperature and the type of goods. In a partly frozen sample a drop in pressure is noted when the point penetrates into the unfrozen portion. For

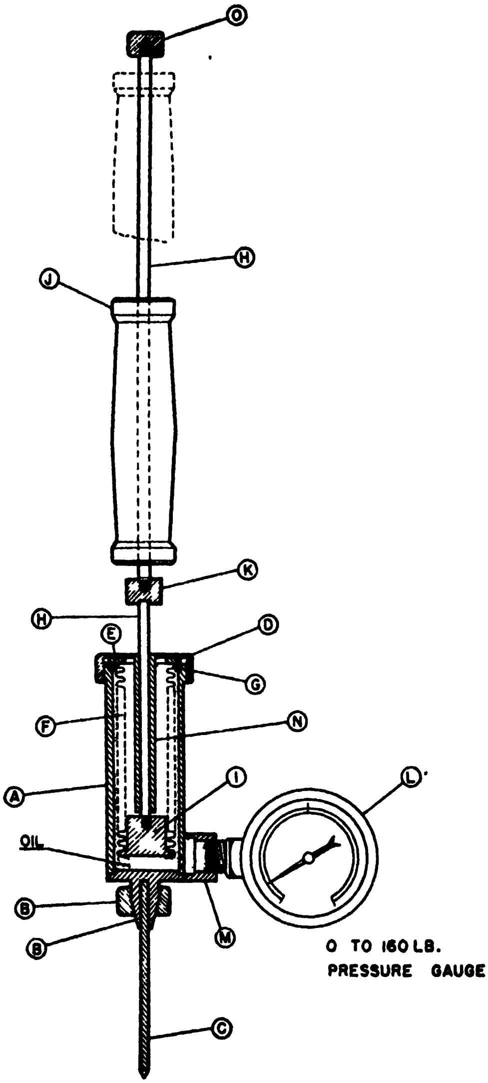

FIG. 1. *Dynamometer for frozen foods.*

example, poultry at 30° F. offers no resistance to the dynamometer, poultry at 20° F. offers about a 50 lb. resistance, and at 0° F. about 160 lb. resistance.

Preliminary trials have indicated that this instrument can be used for inspection work on frozen poultry as a rapid method of detecting unfrozen spots in the center of a carcass. It should be equally useful for determining depth of freezing in other types of frozen flesh, in frozen egg, in fruits frozen in syrup, and in other frozen products.

SOME ELECTROMECHANICAL METHODS FOR PRODUCING LOW FREQUENCIES FROM A PRIMARY FREQUENCY STANDARD[1]

By D. W. R. McKinley[2]

Abstract

Minor mechanical modifications to the clock motor of a quartz crystal primary standard of frequency simplify the problem of producing accurate low frequencies. Electromechanical gate circuits are used to provide pulses of high stability at repetition rates of 1, 10, 100, and 1000 pulses per second for stroboscopic and other applications.

Introduction

The primary standard of frequency at the National Research Laboratories, Ottawa, consists of four temperature-controlled precision quartz crystals and their auxiliary equipment (type C-21-HLD and type 1105-A, General Radio Company). These crystals are checked daily with the official time signals of the Dominion Observatory and with the U.S. Bureau of Standards transmissions. The rates of the crystals are such that a short-term accuracy of 1 part in 10^8 can be guaranteed. The crystal frequency of 50 kc. p.s. is divided by the conventional chain of multivibrators to 10 kc. p.s., 1 kc. p.s., 100 c.p.s., and 10 c.p.s. At the 1 kc.p.s. stage power is furnished to a 1 kc. p.s. phonic motor which rotates at 10 r.p.s. and is geared to drive the hands of a standard clock. There is also a 1 r.p.s. shaft which opens a contactor for about 0.05 sec. each second. This contactor is mounted on a drum, called a microdial, which can be rotated about the shaft to adjust the opening of the contactor to any desired instant in the one-second intervals.

Apart from the standard frequency facilities provided in the spectrum above 50 kc. p.s., which will not be discussed here, the various laboratories require some specific low frequencies for accurate timing applications. The most popular frequency is 60 c.p.s., which unfortunately is incommensurable with the 50 kc. p.s. standard or any of its subharmonics. This 60 c.p.s. frequency was originally obtained by feeding the output of the 10 c.p.s. multivibrator into a double-tripler circuit and filtering the 60 c.p.s. output. The frequency was as accurate as the primary standard when integrated over long periods of time, and was quite satisfactory for clock operation. However, there was a very pronounced jitter of the wave form, due mainly to 10 c.p.s. modulation of the 60 c.p.s. wave, which was never entirely removed even by several sections of filters. This jitter rendered the wave form useless for stroboscopic light devices. Another approach to the problem was more successful. The 1 kc. p.s. output was first tripled to 3 kc. p.s. and then divided by two multivibrator stages to 300 c.p.s. and 60 c.p.s., respectively. The resultant wave

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[2] *Physicist.*

form was free from subfrequency modulation, and operated stroboscopes more satisfactorily. There was still a noticeable jitter present which was due to the inherent locking instability of multivibrators. Each multivibrator in the chain tends to wander a few electrical degrees about a mean locking position. This type of instability can be minimized by good design but can never be eliminated entirely.

At about this time in the development of the standard frequency services the stroboscope requirements were changed. Instead of 60 c.p.s. it was desired to use short impulses with repetition rates of 1, 10, 100, and 1,000 pulses per second. Although simplifying the situation in one sense this new requirement was not immediately attainable owing to the instabilities of the existing chain of multivibrators. Various other techniques were tried to improve the stability, such as the use of blocking oscillators or regenerative dividers, but none has given as good results with a minimum of equipment as the electromechanical gating system to be described.

FIG. 1. *Schematic diagram.*

Resistances, in thousands of ohms

R1	*15*
R2	*15*
R3	*15*
R4	*0 3*
R5	*10*
R6	*0 2*
R7	*75*
R8	*25*
R9	*5*
R10	*500*
R11	*75*
R12	*25*
R13	*50*
R14	*10*
R15	*50*
R16	*500*
R17	*0 2*
R18	*75*
R19	*25*

Potentiometers, in thousands of ohms

P1	*50*
P2	*10*
P3	*25*

Capacitances, in microfarads

C1	*8*	*electrolytic*
C2	*0 2*	*paper*
C3	*25*	*electrolytic*
C4	*8*	*electrolytic*
C5	*1*	*paper*
C6	*0.01*	*paper*
C7	*25*	*electrolytic*
C8	*0 1*	*paper*
C9	*8*	*electrolytic*
C10	*0 01*	*paper*
C11	*0 01*	*paper*
C12	*25*	*electrolytic*
C13	*0.1*	*paper*
C14	*0.01*	*paper*
C15	*0 001*	*mica*
C16	*0 001*	*mica*
C17	*0.01*	*paper*
C18	*0 0005*	*mica*
C19	*25*	*electrolytic*
C20	*0.1*	*paper*
C21	*0 01*	*paper*

Transformers and Inductances

T1	*Audio interstage, modified as in text*
T2	*Audio, 500 ohms to grid*
T3	*Audio interstage*
L1	*Choke, 30 h.*
L2	*500 ohm winding on permanent magnet*
L3	*See L2*

Valves

V1	*6F6, or 6AQ5*
V2	*6AK5*
V3	*1N34*
V4	*6AS6*
V5	*6AL5*
V6	*1N34*
V7	*6AK5*

Production of Standard 60 c.p.s. for Clocks

A six-sector disk of 17 gauge Mu metal, 3 in. outside diameter, was mounted on the 10 r.p.s. shaft of the 1 kc. p.s. phonic clock motor. A slot was cut through the laminations of a small high-impedance audio transformer and the transformer mounted so that the sector disk rotated freely through the slot. A few milliamperes of magnetizing current was drawn through one winding of the transformer from the 200 v. d-c. supply for the clock amplifier (See Fig. 1). As the sectors pass through the slot, the flux variations induce a 60 c.p.s. voltage of a trapezoidal wave form in the other winding of the transformer. The wave form is smoothed by a single-section tuned filter, L1, C2 of Fig. 1, and amplified by V1. This 60 c.p.s. sine wave voltage is made available throughout the laboratories. Individual 200-w. amplifiers are installed locally to avoid difficulties with voltage regulation inherent in a common power amplifier. The 60 c.p.s. wave form is satisfactory for clocks and synchronous motors. The simple sector-disk device has eliminated the

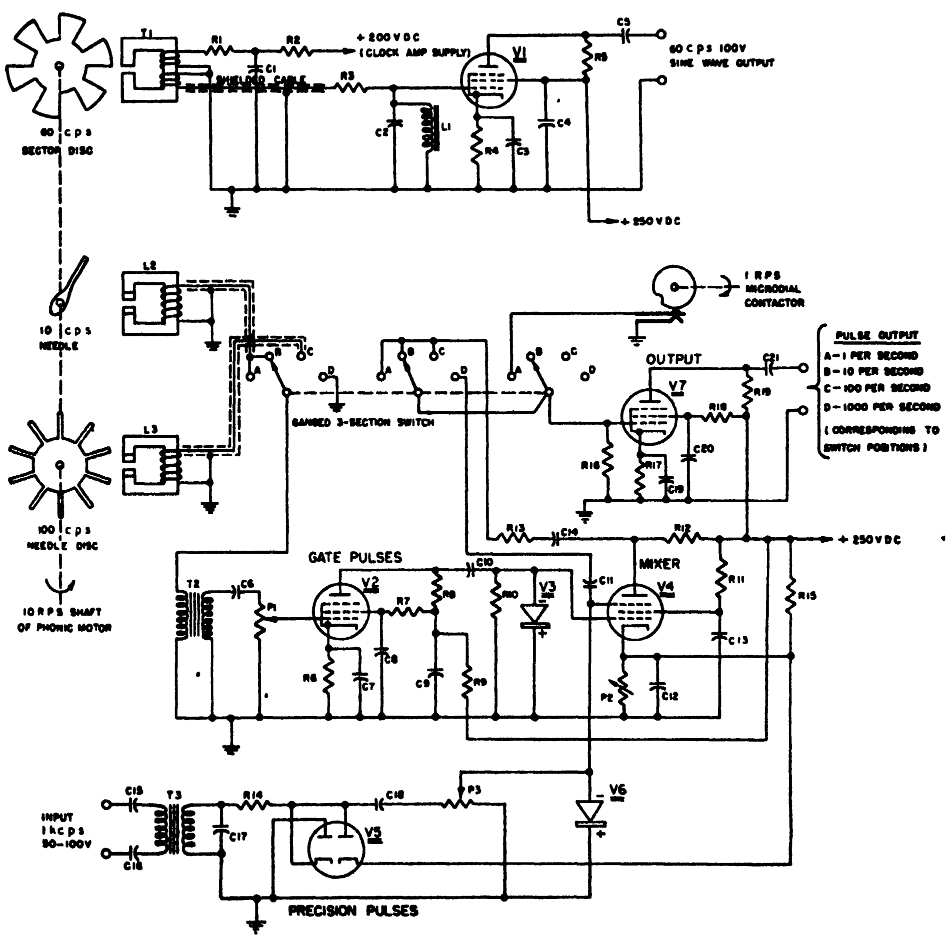

FIG. 1.

10 or 12 vacuum tubes and circuits used in either of the electronic methods described above. The reliability has also improved considerably, because most of the usual faults or failures will affect the amplitude only and not the frequency. This was not always true of the multibrators and other electronic dividers which could sometimes lock on the wrong submultiple after a power-line failure, or run uncontrolled if a circuit failure occurred at an intermediate stage in the chain.

It is true that the phase of the 60 c.p.s. will wander slightly owing to hunting of the 1 kc. p.s. phonic motor. This hunting is usually quite small but can have a maximum amplitude of about $\pm$ 30 electrical degrees at 1 kc. p.s., or about 2 degrees at 60 c.p.s., which is negligible for clock operation although excessive for stroboscopic applications.

Production of Precision Timing Pulses

In addition to the 60 c.p.s. sector disk a narrow strip of 17 gauge Mu metal was also mounted on the 10 r.p.s. shaft of the clock. This strip, or needle, was dynamically balanced to avoid vibration and the tip filed to a square cross section of the thickness of the metal. Another Mu metal disk is provided, which is in effect a small disk carrying 10 accurately spaced needles. The 10 c.p.s. needle and the 100 c.p.s. disk needles each pass through the poles of similar small permanent magnets. The magnets have tapered poles to confine the field to a small angular displacement of the needles. The pickup coils on the magnets have an approximate effective impedance of 500 ohms. Screw-and-slot adjustments are provided for moving the magnets slightly in order to change the phases of the induced voltages.

The voltage pulses induced in the coils by the passage of the needles are not directly usable because they can have a jitter of as much as 80 to 90 μsec., corresponding to the 30 electrical degrees of motor hunting mentioned above. Therefore these pulses are used solely as gate pulses to select, at the desired repetition rate, pulses of much higher timing precision which are produced at the 1 kc. p.s. stage in the counting-down chain.

Fig. 1 is a schematic diagram of the electromechanical system. Suppose, for example, the ganged 3-section selector switch is set at position *B*. The voltage pulses from the 10 c.p.s. needle pickup coil, which have a wave form as shown in Fig. 2 (*a*), are differentiated, amplified, and squared by V2 and its associated circuits. The crystal diode, V3, removes the negative part of the wave so that the wave form at the input to the control grid of the mixer valve V4 is as shown in Fig. 2 (*b*). The dotted wave forms of Fig. 2 (*b*) indicate the probable amount of jitter. The precision timing pulses are then derived from the 1 kc. p.s. clock amplifier by means of the clipping valve, V5, the differentiating circuit, C18, P3, and the crystal diode, V6. The constants of these circuits have been chosen to produce 1 kc. p.s. positive pulses at the suppressor grid of V4 with a sharp rising edge and an approximate duration of 100 μsec. The wave form of these pulses is shown in Fig. 2 (*c*). The cathode bias of V4 is adjusted by means of P2 so that no anode current is

drawn if either the 1 kc. p.s. pulses or the gate pulses are applied separately to the grids of V4. (Incidentally, this positive bias voltage also sets the clipping level of the 1 kc. p.s. pulses.) However, if both the gate pulse and a

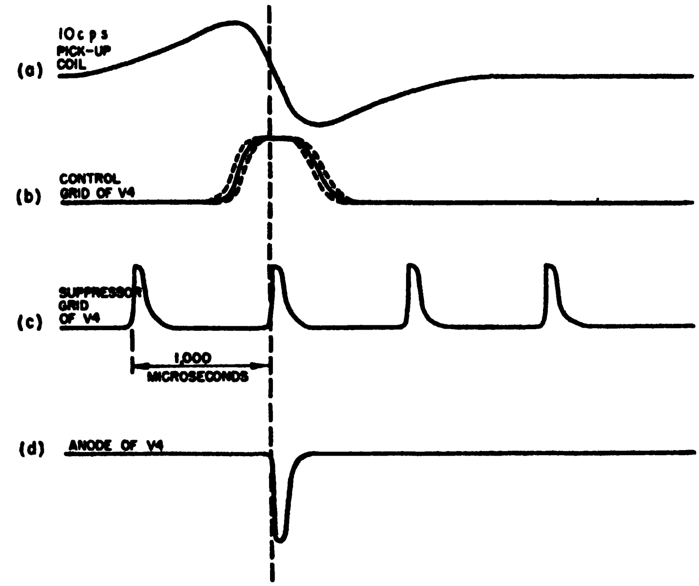

FIG. 2. *Voltage wave forms.*

1 kc. p.s. precision pulse are applied coincidentally to V4, anode current will flow and an anode pulse is produced as shown in Fig. 2 (*d*). The phase of the gate pulse is adjusted mechanically to ensure that the gate will straddle the precision pulse. The output of V4 is then amplified by V7 to about 100 peak volts. Thus the output pulses are actually the same pulses as supplied to the suppressor grid of V4 but selected at a rate of 1 in 100, or 10 per sec. The timing precision of these pulses is the same as that of the original 1 kc. p.s. source and is not affected by jitter of the gate pulse.

If the selector switch is now set to position *A* the microdial contactor will ground the grid of V7 except over a period of approximately 0.05 sec. each second. This gate, which is considerably wider than a single pulse but not wide enough to include two 10 c.p.s. pulses, can be phased by the microdial to straddle one of the output pulses. The over-all rate is now 1 in 1000 or one pulse per second.

Putting the selector switch on position *C* simply connects the input of V2 to the 100 c.p.s. needle disk. The operation is the same as described above for position *B* except that the output pulses are now selected at the rate of 1 in 10 or 100 pulses per second.

When the selector switch is in position *D* the mixer tube V4 is by-passed and the precision pulses are supplied directly to the output stage at a rate of 1000 pulses per second. The output pulses in this case will be negative,

whereas the pulses produced at switch positions A, B, and C, are positive, owing to the inversion occurring in V4. A single triode push-pull inverter stage could be added to the output to provide low-impedance positive or negative pulses as desired, but this feature was not required in the laboratory.

When examined on a high-speed osilloscope it is seen that the 1 kc. p.s. precision pulses produced from the 1 kc. p.s. standard frequency source actually have a small jitter of the order of a microsecond or less, representing an interval timing error of one part in a million at one pulse per second. The uncertainty in the triggering of stroboscope tubes is rather greater than this, so the stability of the pulse is fully adequate for these purposes. This residual jitter is attributable to the characteristics of the 10 kc. p.s. and 1 kc.p.s. multivibrators. If it is desired to produce pulses at low repetition rates with jitters of the order of 0.1 or even 0.01 μsec. it will be necessary to form the pulses at the crystal frequency and then to gate these pulses electronically at 10 kc. p.s. and 1 kc. p.s. For example, this can be done by using the existing multivibrators solely to provide gating pulses to mixer circuits, similar to that shown in Fig. 1, at the 10 kc. p.s. and 1 kc. p.s. levels. The resultant pulse produced at the one pulse per second level, say, will have an extremely small jitter but the pulse will necessarily be quite short, of the order of 1 or 2 μsec., and some lengthening may be required to make it usable in practical timing applications.

The electromechanical gating technique described above is applicable to any of the usual types of quartz crystal primary or secondary standards incorporating an electric clock at some stage in the frequency division chain, and it offers several advantages over purely electronic methods below 1 kc. p.s. in simplicity of apparatus, reliability of operation and maintenance of precision.

Acknowledgment

Mr. W. E. M. Dale built and installed the circuit elements, and the mechanical parts were prepared by the staff of the machine shop under Mr. I. L. Newton.

OBSERVATIONS ON THE ADSORPTION OF WATER VAPOR BY WHEAT[1]

By J. D. Babbitt[2]

Abstract

The adsorption and desorption of water vapor by wheat was measured by means of a McBain sorption balance. Curves are obtained showing the rate at which moisture is adsorbed by kernels of wheat directly exposed to a humidified atmosphere, and a theory is advanced to account for the rate of adsorption. It is shown that the rate of adsorption is governed largely by the time taken for the moisture to diffuse up to the surface of the wheat. Under storage conditions, this is much greater than the time required for the moisture to penetrate the kernel of wheat from its surface.

The Adsorption Isotherm

Several observers (4, 6, 7) have measured the water vapor adsorption isotherm for wheat, but no provision was made in any of the measurements to distinguish between adsorption and desorption and no measurements were recorded on wheat of low moisture content. In order to study the difference between adsorption and desorption and to observe the behavior at low moisture contents some measurements were made with wheat by means of a McBain sorption balance. Preliminary results have already been published (2) but more extensive data are now available and are worth recording.

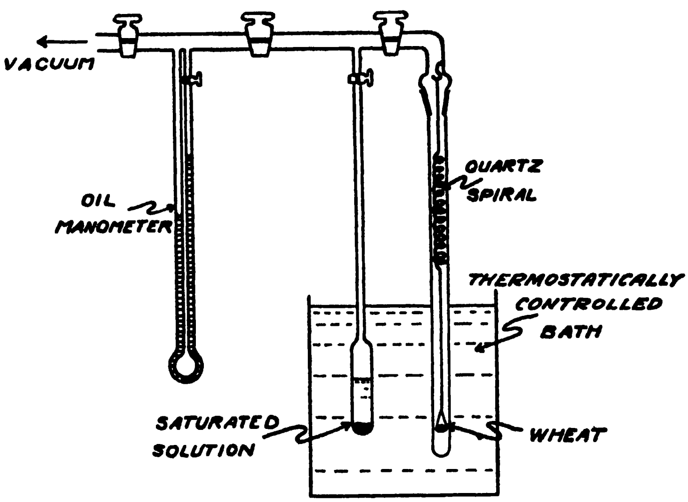

Fig. 1. *Adsorption apparatus.*

The arrangement of the apparatus is shown in Fig. 1. The wheat (approximately 10 kernels) was suspended on a quartz spiral in a glass tube. A

Manuscript received September 27, 1948.

[1] *Contribution from the Division of Physics, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1882.*

[2] *Physicist.*

saturated salt solution, held at a constant temperature by the same water bath that surrounds the wheat, maintained a constant relative humidity in the glass tube, and various humidities were obtained by using different salts. The air was evacuated from the system so that all measurements were made in an atmosphere of water vapor alone. The vapor pressure was measured by means of a manometer containing a vacuum oil having a low vapor pressure. The extension of the spiral spring was measured with a cathetometer and the spring was calibrated by the use of standard weights.

To determine an isotherm, the wheat, which had been previously dried, was placed on the balance and the apparatus evacuated. The extension of the spring, as then measured, corresponded to the dry weight of the wheat. The system was then opened to the saturated solution and the extension of the spring measured at intervals until there was no further elongation. At the same time the pressure as given by the manometer was recorded. In some observations, measurements were continued over several days in order to be certain that the adsorption was complete. The moisture content was calculated from the extension of the spring, and the vapor pressure was obtained from the manometer reading. When an observation at one relative humidity was completed, the solution was changed and the procedure repeated. In this way the complete isotherm was obtained.

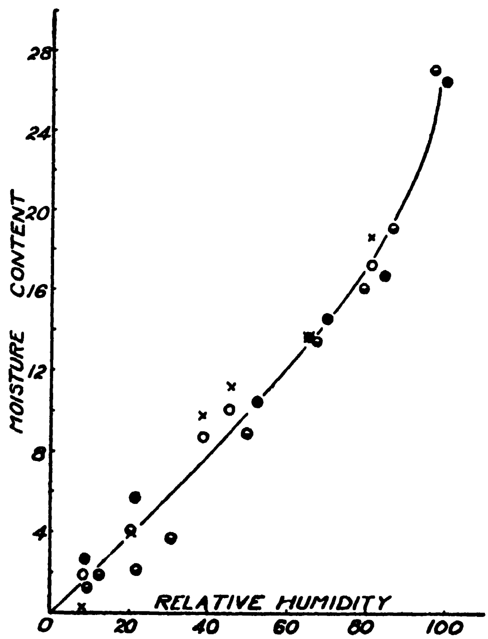

FIG. 2. *Adsorption isotherm. 25° C.*

The results of the measurements on adsorption are collected in Fig. 2 while those for desorption are given in Fig. 3. Throughout this paper the moisture content is expressed as percentage of the dry weight of the wheat.

The wheat used was, in one experiment, No. 1 Northern Garnet wheat and in the others No. 1 Northern Marquis wheat. It was not intended in these experiments to study the difference in behavior of various varieties of wheat but only to observe the general nature of the adsorption.

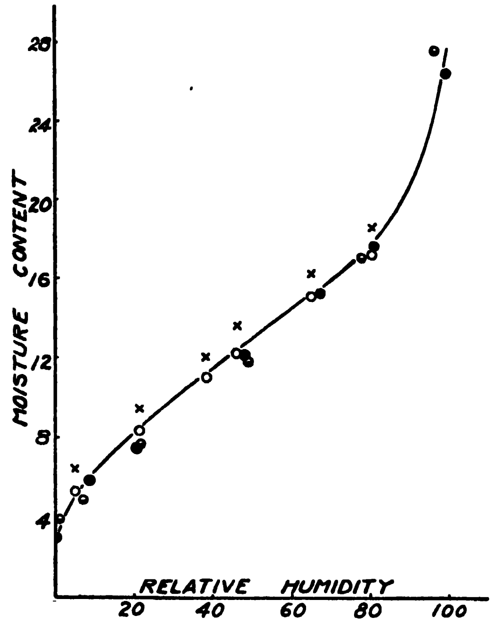

FIG. 3. *Desorption isotherm.*

For both adsorption and desorption there is considerable scatter in the results, but it should be noted that for a series of readings on any one sample the points for desorption appear to give a more consistent curve than those for adsorption; for any one series of points in Fig. 3 a smooth sigmoid curve is obtained but for adsorption this is not so. In Fig. 2 the experimental points are scattered uniformly about a mean curve and each series of measurements does not have the continuity that is found in desorption.

At low moisture contents the curve for adsorption is convex to the humidity axis and there is no indication of the concave curvature that is often found for adsorption by organic materials and that is clearly shown in the desorption curve. One set of measurements (represented by ●) does indicate such a curvature but this is not substantiated by the other measurements. The individual points for desorption for each sample of wheat lie on a fairly smooth curve although the curves for different samples do not exactly coincide. There is no doubt that the desorption curves have a definite reversal of curvature and are strongly concave to the relative humidity axis at low moisture contents.

It is difficult to say why the behavior of the wheat should differ in this way during adsorption and desorption. The deviation of the individual points

from a smooth curve could have been caused by fluctuations in the vapor pressure; small variations in the temperature of those parts of the apparatus not in the thermostat, or failure of the solution to attain uniform saturation, might change the vapor pressure over a short interval of time sufficiently to give an altered moisture content and, owing to hysteresis, this spurious moisture content would remain when conditions became normal. That this should have occurred during adsorption and not during desorption is improbable. There are other reasons to believe, moreover, that these differences are not the result of fluctuations in the vapor pressure; in several of the experiments two balances were used and yet there was no correlation in the deviations for two samples of wheat even when exposed to the same atmosphere of vapor. Also, in an experiment in which wheat was exposed on one balance and flour on the other, it was found that deviations that occurred for the wheat did not occur for the flour. The measurements made on a sample of flour are shown in Fig. 4. It should be noted that the hysteresis is less pronounced than for wheat and the curve for adsorption is concave to the humidity axis at low moisture contents.

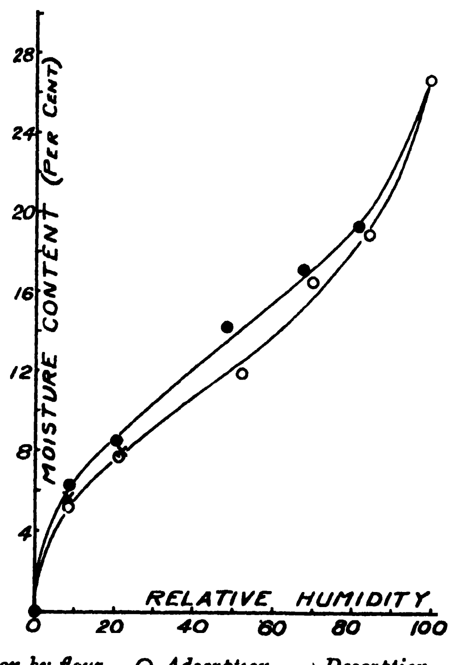

FIG. 4. *Adsorption by flour.* ⊙ *Adsorption.* ı *Desorption.* × *Second adsorption.*

With the exception of one run at 34° C. (Fig. 5) the experiments were carried out at a temperature of 25° C. At 34° C. it was impossible to take the measurements to high relative humidities, as under these conditions condensation occurred in the parts of the apparatus that were at room temperature.

In completing the desorption curve it was never possible to remove all the moisture from the wheat. To obtain zero relative humidity, the apparatus

was evacuated with a mercury diffusion pump. After days of evacuation the wheat still retained several per cent of moisture and no appreciable change of moisture content occurred from one day to the next. This residual moisture

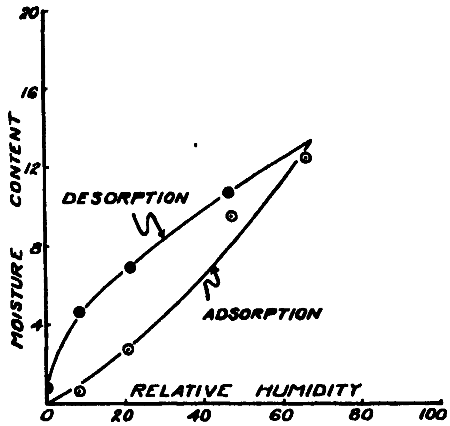

FIG. 5. *Isotherm for wheat at 34° C.*

content is shown graphically by the fact that in Fig. 3 the desorption curve for 25° C. cuts the axis at approximately 3% moisture content. The effect for the curve at 34° C. is less pronounced; throughout its length the desorption branch is below that for 25° C. and the residual moisture content is only 0.8%. Thus it is evident that the residual moisture content is a function of temperature. With the flour the moisture was completely removed by evacuation.

There was some question whether this residual moisture content was real; the difference between the final and original weight might represent an addition to the dry weight of the wheat caused by the cycle of moisture changes to which it had been exposed. That it was a true residual moisture content was shown by the following. A sample of wheat that had undergone a desorption cycle and after evacuation had retained some residual moisture was exposed to an increasing series of relative humidities so that a second adsorption curve was obtained. When the relative humidity had increased to 20% the moisture content was equal to that obtained in the original adsorption measurements. An additional proof is given by the fact that the wheat when removed from the apparatus and dried to constant weight in a vacuum oven had the original dry weight.

The Time-Rate of Change of Moisture Content

Introduction

The time required for the moisture content of wheat to come to equilibrium with any relative humidity to which it is exposed is not only of scientific interest but also, owing to the influence of moisture content on the keeping quality of wheat, of great commercial importance. Many factors influence

the rate at which water vapor is adsorbed by wheat and this is especially true when the kernels are not isolated but are confined within the bulk of a mass of wheat. It is obvious that a single kernel of wheat directly exposed to water vapor will take up moisture more quickly than kernels several inches below the surface in a grain elevator. On account of the resistance of air to the movement of water vapor one would expect that the rate of approach to equilibrium would be slower in air than in an atmosphere having the same water vapor pressure but from which the air has been exhausted. If, however, the air is maintained in rapid motion the water vapor at the surface of the kernel will be replenished as fast as it is adsorbed and the rate of adsorption will more nearly equal that of vapor alone. In studying the rate at which moisture is taken up by wheat it is important to distinguish between the effect of the diffusion of the water vapor through the air and the surrounding wheat up to the surface of the kernel from the diffusion through the skin and into the kernel itself. Before describing some experiments that were devised to disentangle these effects it is necessary to discuss the fundamentals of diffusion theory.

Fundamentals of Diffusion

If the coefficient of diffusion is defined as the ratio of the total mass that flows across unit area of any small section in unit time to the rate of decrease of density per unit distance in a direction perpendicular to that section, the fundamental equation of diffusion is

$$\frac{dQ}{dt} = -D\frac{d\rho}{dx}\,dydz\,, \tag{1}$$

where dQ is the mass passing through a plane of area $dydz$ in time dt, D is the coefficient of diffusion, and $\frac{d\rho}{dx}$ the density gradient.

From this fundamental equation, the differential equation governing diffusion (Fick's law) may be derived in a manner similar to that by which Fourier's equation is obtained in the analogous phenomenon of heat flow. We consider the flow of matter into and out of a differential block through the two faces normal to the direction of the x-axis, and obtain

$$\begin{aligned}\left(\frac{\partial Q}{\partial t}\right)_x &= -\left(D - \frac{1}{2}\frac{\partial D}{\partial x}dx\right)\frac{\partial}{\partial x}\left(\rho - \frac{1}{2}\frac{\partial\rho}{\partial x}dx\right)dy\,dz\\ &\qquad + \left(D + \frac{1}{2}\frac{\partial D}{\partial x}dx\right)\frac{\partial}{\partial x}\left(\rho + \frac{1}{2}\frac{\partial\rho}{\partial x}dx\right)dy\,dz\\ &= \left(D\frac{\partial^2\rho}{\partial x^2} + \frac{\partial D}{\partial x}\frac{\partial\rho}{\partial x}\right)dx\,dy\,dz\,.\end{aligned}$$

But since $\left(\frac{\partial Q}{\partial t}\right)_x = \left(\frac{\partial\rho}{\partial t}\right)_x dx\,dy\,dz$

$$\begin{aligned}\left(\frac{\partial\rho}{\partial t}\right)_x &= D\frac{\partial^2\rho}{\partial x^2} + \frac{\partial D}{\partial x}\cdot\frac{\partial\rho}{\partial x}\\ &= D\frac{\partial^2\rho}{\partial x^2} + \frac{\partial D}{\partial\rho}\cdot\frac{\partial\rho}{\partial x}\cdot\frac{\partial\rho}{\partial x}\\ &= D\frac{\partial^2\rho}{\partial x^2} + \frac{\partial D}{\partial\rho}\cdot\left(\frac{\partial\rho}{\partial x}\right)^2 - - - \,.\end{aligned} \tag{2}$$

By similar considerations in the y and z directions we get for the equation in three dimensions

$$\frac{\partial\rho}{\partial t} = D\,\nabla^2\rho + \frac{\partial D}{\partial\rho}\,(\text{grad}\;\rho)^2\,. \tag{3}$$

This is the exact differential form of Fick's law. If D is independent of the concentration the second term is zero and we have the simple form which has been solved for most of the common geometrical shapes and is, therefore, generally used.

In experimental work on gases, the pressure, rather than the concentration, is measured and quite commonly the diffusion coefficient is expressed as the mass flow per unit pressure gradient. For gases in free space, where the concentration is linearly proportional to the pressure, the use of the pressure rather than the concentration gradient is equivalent to multiplying D by a constant factor. When, however, we come to study the diffusion of gases through solids the pressure is not always proportional to the density, for all the complications associated with adsorption are present; it is exceedingly rare to find any substances for which the amount of material adsorbed is linearly proportional to the pressure, and before applying the pressure gradient to the diffusion equation it is necessary to develop the appropriate equation from fundamentals.

We start by writing the fundamental Equation (1) in terms of a second diffusion coefficient D_p, which bears to the pressure gradient the same relation that D bears to the concentration gradient.

$$\frac{dQ}{dt} = -\,D_p\,\frac{dp}{dx}\,dy\,dz\,, \tag{4}$$

and proceeding as before we develop the differential equation in terms of the pressure.

$$\left(\frac{\partial\rho}{\partial t}\right)_x = D_p\,\frac{\partial^2 p}{\partial x^2} + \frac{\partial D_p}{\partial p}\left(\frac{dp}{dx}\right)^2\,. \tag{5}$$

This may be written

$$\frac{\partial\rho}{\partial p}\left(\frac{\partial p}{\partial t}\right)_x = D_p\,\frac{\partial^2 p}{\partial x^2} + \frac{\partial D_p}{\partial p}\left(\frac{\partial p}{\partial x}\right)^2\,. \tag{6}$$

In considering the diffusion of a gas such as water vapor through an adsorbing material such as wheat the concentration ρ would be the weight of water vapor per unit volume. In adsorption, however, the moisture content is commonly expressed as the weight adsorbed per unit weight of dry adsorbent. If m is the moisture content and μ the density of the dry adsorbent we have

$$\rho = m\,\mu\,,$$

and

$$\frac{\partial\rho}{\partial p} = \mu\,\frac{\partial m}{\partial p}\,.$$

Now $\frac{\partial m}{\partial p}$ is the slope of the adsorption isotherm and following Daynes (5) we shall call it the specific solubility and denote it by S. Then

$$\frac{\partial \rho}{\partial p} = \mu S , \tag{7}$$

and Fick's law has the form

$$\mu S \left(\frac{\partial p}{\partial t}\right)_x = D_p \frac{\partial^2 p}{\partial x^2} + \frac{\partial D_p}{\partial p}\left(\frac{\partial p}{\partial x}\right)^2 . \tag{8}$$

In three dimensions

$$\mu S \frac{\partial p}{\partial t} = D_p \nabla^2 p + \frac{\partial D_p}{\partial p} (\text{grad } p)^2 \tag{9}$$

In order to find the relation between the two coefficients D and D_p we take the two fundamental equations

$$\frac{dQ}{dt} = - D \frac{d\rho}{dx} dy\, dz$$

and

$$\frac{dQ}{dt} = - D_p \frac{dp}{dx} dy\, dz .$$

If $\frac{dQ}{dt}$ is the same in both equations we must have

$$D \frac{d\rho}{dx} = D_p \frac{dp}{dx} ,$$

and

$$D_p = D \frac{d\rho}{dp}$$

$$= D \mu S . \tag{10}$$

We have already mentioned the analogy between the equations of diffusion and those of thermal conductivity; Equation (10) is analogous to the relation between the thermal conductivity k and the thermal diffusivity κ. In Fourier's equation we find

$$\kappa = \frac{k}{dc} ,$$

where d is the density and c the specific heat. It is evident, therefore, that D corresponds to the thermal diffusivity, D_p to the thermal conductivity, and S to the specific heat. The pressure p is the potential function corresponding to the temperature.

Rate of Approach to Equilibrium in Wheat

The movement of water vapor into wheat can be studied by exposing wheat to an atmosphere of constant relative humidity and measuring the change of weight with time. With this idea in mind several different types of experiments were carried out. In some a small quantity of wheat was placed in a weighing bottle and exposed in a desiccator to an atmosphere of constant humidity; in other experiments the weighing bottle with the wheat was exposed in a small chamber, which was maintained at constant temperature and humidity and in which the air was rapidly circulated by means of a

fan; in one single experiment the approach to equilibrium was measured on one of the sorption balances used in the experiments described in the first part of this paper. In all experiments, saturated salt solutions were used to obtain a constant humidity, and sodium chloride, which gives a relative humidity of 75%, was the solution employed in the majority of the experiments.

As previously mentioned there are two aspects of adsorption that must be considered; first, there is the diffusion of the water vapor from the solution to the surface of the wheat and, secondly, there is the diffusion through the skin and into the kernel. The preliminary experiments were designed to eliminate the effect of diffusion through the air and to obtain as closely as possible an estimate of the time required for the moisture to penetrate the kernel from its surface. The wheat was, therefore, exposed in a single layer so that no superimposing wheat was present to restrict the movement of the moisture up to the wheat.

The results obtained from some of the experiments with single layers of wheat are reproduced in Fig. 6. The curves in this graph show that the

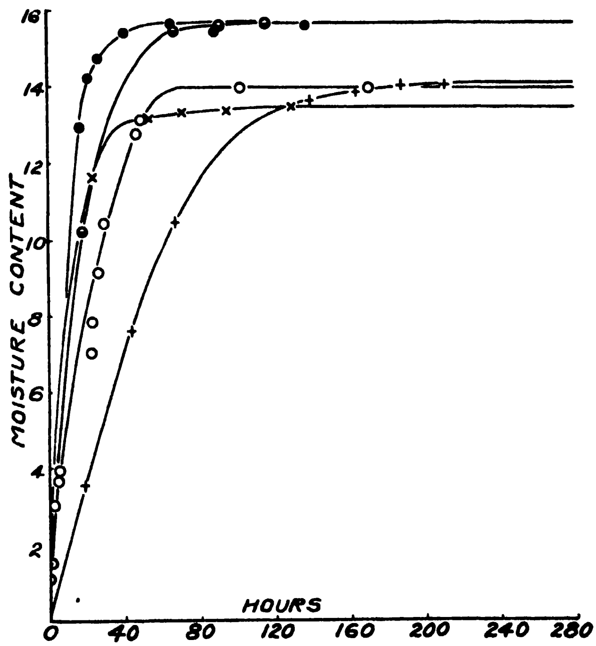

FIG. 6. *Rate at which moisture is adsorbed by single layers of wheat under various conditions.* ○ *Sorption balance in vacuum* × *Humidity chamber with fan.* ● *Humidity chamber with fan.* ◒ *Humidity chamber with fan* + *Desiccator.*

moisture content increased most rapidly for the wheat that was exposed in the humidity chamber with a fan blowing the air over the surface of the kernels, and least rapidly for the wheat in the desiccator. The wheat on the sorption balance adsorbed the moisture at a rate slightly less than that in

the humidity chamber; one might have expected the adsorption on the balance to proceed more quickly since it took place in an atmosphere of water vapor with no air present to resist the movement of the moisture. There was, however, considerable glass tubing between the solution and the wheat, and this may have substantially delayed the movement of the moisture. The evaporation of the moisture from the surface of the solution may also have been slower in this apparatus since in the humidity chamber the air was directed across the surface of the solution by the fan. The final equilibrium value was not the same in all these experiments, owing to differences in the wheat or variations in the relative humidity, but nevertheless the differences in the rate of approach to equilibrium are obvious.

From these experiments we are entitled to assume that in the humidity chamber the time required for the wheat to reach the equilibrium moisture content is almost completely the result of the resistance to diffusion within the grain itself; that is, we can assume that the rapid circulation of air ensures that at the surface of the wheat the air will contain water vapor in the concentration corresponding to the equilibrium conditions.

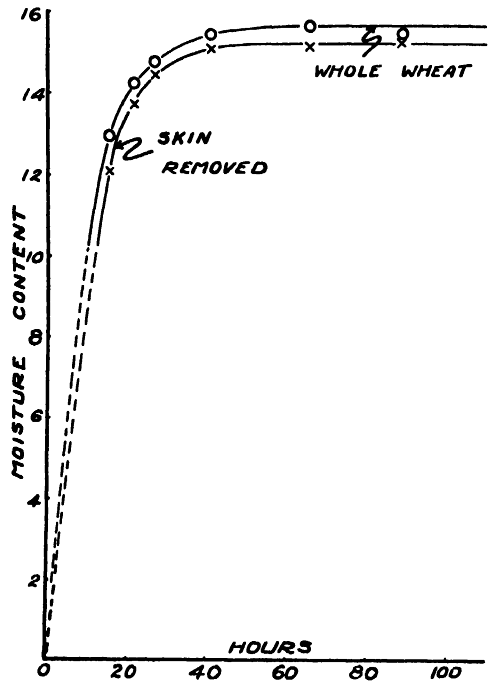

FIG. 7. *Comparison of adsorption by wheat with and without skin.*

As a preliminary consideration it would be natural to assume that the greater part of the resistance to the movement of moisture into the grain resided in its skin (pericarp). In order to test this assumption the skin was removed from several kernels and these were exposed to a moist atmosphere under similar conditions to some whole grains. The results are shown in

Fig. 7. Allowing for the fact that there is a slight difference in the final equilibrium moisture content, the approach to equilibrium is almost identical. The indication is that the skin offers little resistance to the movement of moisture.

Calculation of Rate of Approach to Equilibrium

If we assume that a kernel of wheat is a sphere of homogeneous material and that, under the driving force of the concentration gradient, the moisture diffuses into the sphere according to Fick's law we can calculate the shape of the moisture content versus time curve. Thus if C_0 is the initial concentration in a sphere and C_2 the concentration at the surface, the amount Q_t that has diffused into the sphere in time t is given by

$$Q_t = -(C_2 - C_0)\frac{4\pi a^3}{3}\left[1 - \frac{6}{\pi^2}\sum_1^{\infty}\frac{1}{n^2}e^{-D\frac{n^2\pi^2 t}{a^2}}\right], \tag{11}$$

where a is the radius of the sphere. (For derivation of this formula see: "Diffusion in and Through Solids," by R. M. Barrer; Cambridge University Press, 1941, page 29. In this book there is a mistake in the constant.) This equation has been derived from the concentration form of Fick's law and the coefficient D is the true diffusion constant. D has the dimensions of L^2/T.

To adapt this equation for our purpose we replace the concentrations with the corresponding moisture contents and put $Q_t = \dfrac{4\pi a^3 m}{3}$, where m is the average moisture content throughout the kernel at the time t. For convenience we write $D\dfrac{\pi^2}{a^2} = D'$. We assume that $m_0 = 0$ and that the moisture content m_2 at the surface of the sphere is the same as the final moisture content. Then we have

$$m = m_2\left[1 - \frac{6}{\pi^2}\left(e^{-D't} + \frac{1}{4}e^{-4D't} + \frac{1}{9}e^{-9D't} + \dots\right)\right]. \tag{12}$$

To test this equation we use the curve for wheat in the humidity chamber with the fan blowing. We evaluate D' by taking the point $t = 20$ hr., $m = 14.00$, and obtain $D' = 0.087$. Using this value of D' we can calculate the whole curve. This is shown in Fig. 8; the fit with the observed results is fairly good but although the curves are similar in shape there are indications that the observed values rise more slowly at the beginning and more rapidly at the end than the calculated values. The calculated values are based on a diffusion coefficient D which remains constant throughout the adsorption; the observed results indicate that D increases as the moisture content of the grain increases.

Several workers have pointed out that at low moisture contents vapors diffuse through adsorbing materials much more slowly than at high moisture contents. In addition there is a secondary effect that may exert considerable influence on the adsorption. We have shown in Equation (10) that the concentration coefficient is related to the pressure coefficient by the relation

$D = D_p/\mu S$ and is thus inversely proportional to the specific solubility S. The specific solubility, which is the slope of the adsorption isotherm, increases with humidity, as is clearly shown in Fig. 2. As S increases, the

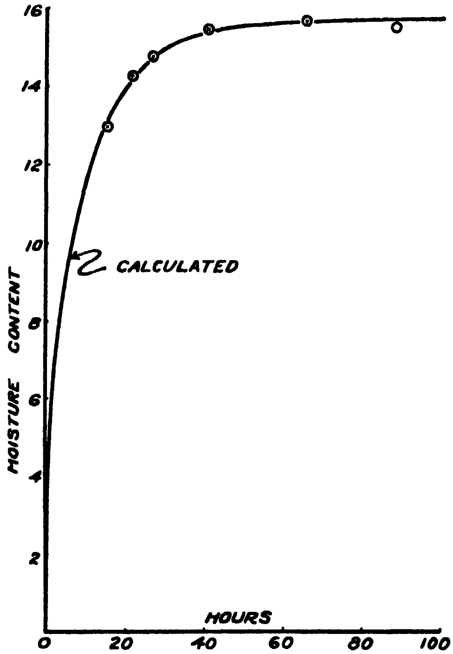

FIG. 8. *Comparison of calculated with observed rate of adsorption.* ⊙ *Observed.*

diffusion coefficient D should decrease. Since experimentally we find that, during adsorption, D actually seems to increase we can only infer that the effect of the specific solubility S is masked by a greater change in the coefficient D_p.

When we study the drying of wheat, the effect of the variation in the coefficient is more pronounced. To study this, the process described above was reversed; wheat having a moisture content around 15% was exposed to a dry atmosphere. In all but one of these desorption experiments the wheat was exposed in a desiccator and the air was still. In one experiment the desiccator was evacuated. Although we have already seen from Fig. 6 that the exchange of moisture is considerably delayed by the resistance of the air yet by comparing the desorption with adsorption under similar conditions we can readily see the differences in the two processes.

In Fig. 9 the results of two desorption experiments with single layers of wheat are shown and two adsorption curves have been reproduced for comparison. There are two important factors that distinguish the desorption from the adsorption curves; the desorption curves do not reach an end point and there appears to be a residual moisture content that would not be removed even after an infinite length of time. One of the desorption curves was

obtained with the wheat in an evacuated desiccator and the other with the wheat in a desiccator at atmospheric pressure. There is little difference in the rate of desorption and the difference that is shown may well be explained

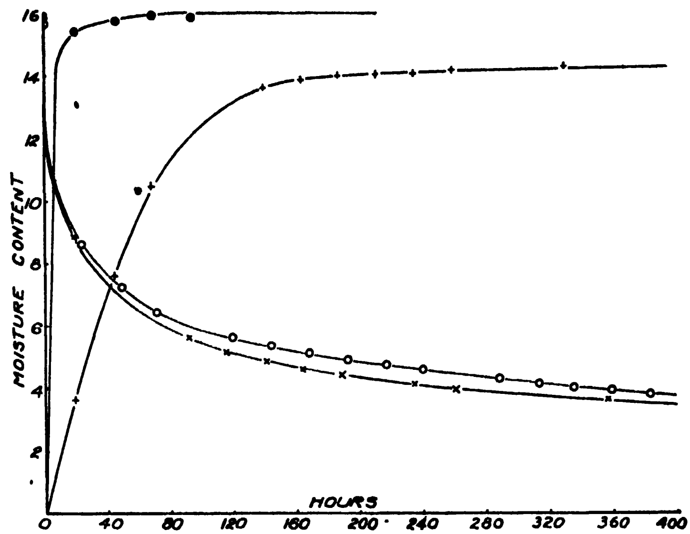

FIG. 9. *Comparison between adsorption and desorption.* ○ *Desorption in vacuum desiccator at room temperature.* × *Desorption in desiccator at 91 3° C.* ● *Adsorption in humidity chamber with fan.* + *Adsorption in desiccator.*

by a difference in temperature. The desorption in the evacuated desiccator should be comparable to the adsorption under the most rapid conditions, and a curve showing the adsorption with a fan blowing a current of air across the wheat is reproduced. The second adsorption curve was obtained with the wheat in a desiccator containing a saturated sodium chloride solution under still air conditions. In the initial stages there is some resemblance between this adsorption curve and the desorption curves but the adsorption curve, and this occurs in all experiments, does come to a definite end point. The difference in the shape of the adsorption curve obtained with the air in rapid motion is most pronounced. There the adsorption rises rapidly and decisively to an end point.

The fact that it is impossible to remove all the moisture from wheat at room temperatures by evacuation or desiccation has already been noticed in the experiments with the sorption balance. There it was also found that if the temperature was raised the residual moisture content was lowered. To elucidate this point, desorption curves were obtained at higher temperatures. These are shown in Fig. 10. The curves were obtained with wheat under atmospheric pressure in a desiccator. The effect of increase of temperature is readily apparent, the initial loss of moisture being more rapid and the final values lower. In all curves there is still a finite decrease in the moisture content at the conclusion of the experiments. It is impossible to say whether this decrease would go on indefinitely and whether the wheat would finally

attain zero moisture content. It is evident, however, that at some temperature (perhaps the boiling point of water) all the water vapor would be removed; this is a basic assumption in this work, as the final weight obtained in a vacuum oven has been taken as the dry weight of the wheat.

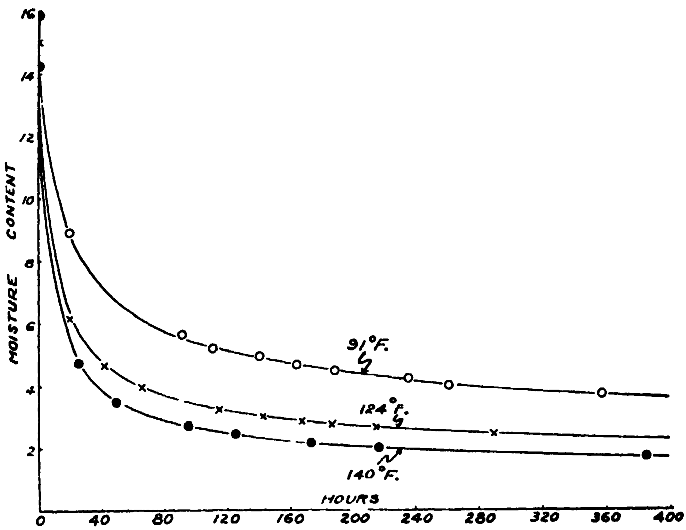

FIG. 10. *Effect of temperature on desorption.*

The difference in the behavior of the wheat during adsorption and desorption might have been forecast from the differences in the adsorption and desorption isotherms. We have pointed out that the diffusion coefficient D is equal to $\frac{D_p}{\mu S}$ and is therefore inversely proportional to the specific solubility. In the desorption curves, on account of the reverse curvature, the slope is very large at low moisture contents and becomes infinite as we approach the origin. D, therefore, becomes small and the desorption would proceed very slowly. The behavior of D during desorption can be seen more clearly if we attempt to fit the experimental curve with Equation (12). For desorption this has the form

$$m = m_0 - (m_0 - m_2)\left[1 - \frac{6}{\pi^2}\sum_1^\infty \frac{1}{n^2}\, e^{-n^2D't}\right], \qquad (13)$$

in which m_0 is the initial and m_2 the final moisture content. Since the end point is not zero we have to assume an appropriate value for m_2.

The values calculated from this equation for the curve at 91.3° F. are shown in Fig. 11; $m_0 = 15.90$, $m_2 = 3.40$, and D' was found to be equal to 0.014. To determine D' the calculated values were made to fit the experimental values at $t = 100$. It is immediately seen that the desorption is more rapid at the beginning and less rapid at the end than that given by the equation It should also be noted that the equation gives a constant value for the moisture content after 400 hr., while the experimental results are

still decreasing at this point and give no indication of reaching an equilibrium value. The difference between the calculated curve and the experimental points is strong evidence that D' is decreasing throughout the experiment.

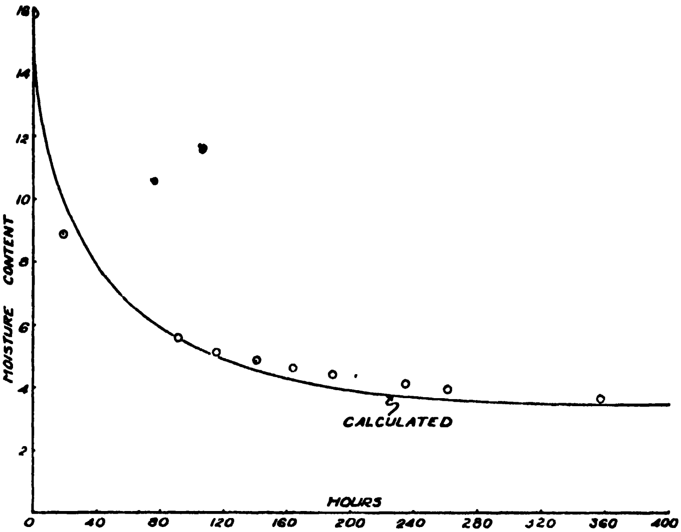

FIG. 11. *Relation between observed and calculated values for desorption:* ⊙ *Observed values.*

We have stated that the low value of D' at low moisture contents is the reason for the slow approach to equilibrium. This low value of D' results from the high curvature of the desorption curve near the origin. In order to

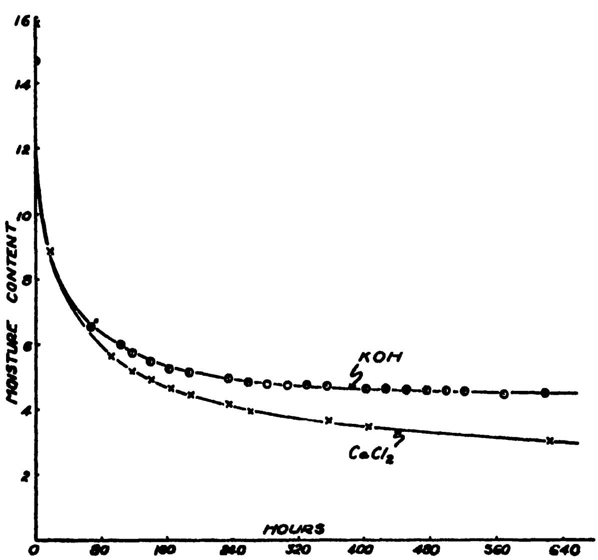

FIG. 12. *Difference in desorption with potassium hydroxide and calcium chloride.*

show the effect of this, two desorption experiments were made under similar conditions, in one of which the desiccant was calcium chloride and in the other potassium hydroxide. Potassium hydroxide gives a relative humidity of approximately 9% and, according to Fig. 3, the specific solubility would be finite in that region. We should expect the moisture in the wheat exposed to potassium hydroxide to reach a definite end point, in contrast to the behavior usual with calcium chloride. That such is the result is shown in Fig. 12. The desorption with potassium hydroxide, while proceeding at the beginning at a rate not much slower than that with the calcium chloride, does appear to have reached an end point at 600 hr., while the other curve gives no such indication.

Experiments on Adsorption in Depth

It has already been pointed out that when wheat is present in bulk one would expect that kernels in layers below the surface would pick up moisture much more slowly than those on the surface, and that consequently dry wheat exposed to humidity would not attain equilibrium throughout its depth for a considerable length of time. Some evidence of this effect has already been shown by the difference in the time required for wheat to adsorb moisture when exposed in still air in contrast to a vacuum or rapidly moving air. One would expect the presence of other wheat kernels, which makes it necessary for the moisture to diffuse through the interstices between the grains, to increase this effect and to reduce the rate of adsorption to a very low value. That such is the result is shown by some simple experiments.

Small samples of wheat were placed in cylindrical glass vessels approximately $1\frac{1}{2}$ in. in diameter. The height of the vessels and the depth of the wheat varied in the different experiments. In a constant-temperature chamber, the samples were exposed at the top surface to a constant relative humidity of 75% with a fan blowing over the surface of the wheat.

The results are shown in Fig. 13. The measurements were made for a period of 400 hr. The abscissae are the amounts of moisture adsorbed expressed as a percentage of the total weight of wheat. As the depth of the wheat becomes greater the percentage of moisture adsorbed during any period becomes smaller. It is obvious that the adsorption would not be uniform throughout the wheat but that the kernels on the surface would be close to the equilibrium value, while those deep in the vessel would have taken up a very small amount of moisture. If the experiments were carried on for a sufficient length of time all the wheat throughout the vessel would ultimately arrive at the equilibrium moisture content, and the rate at which it approaches equilibrium gives a measure of the slowness of diffusion through wheat.

It is evident from these curves that water vapor can move through wheat only very slowly. Even so little as an inch of wheat has retarded the adsorption to such an extent that the process is only just complete at the end of 400 hr. With a depth of 6 in. the process is only a third completed at the

end of this period and, since the rate of the process gets progressively slower as equilibrium is approached, it is obvious that it would require a very long period indeed before the whole of the wheat had reached the equilibrium moisture content.

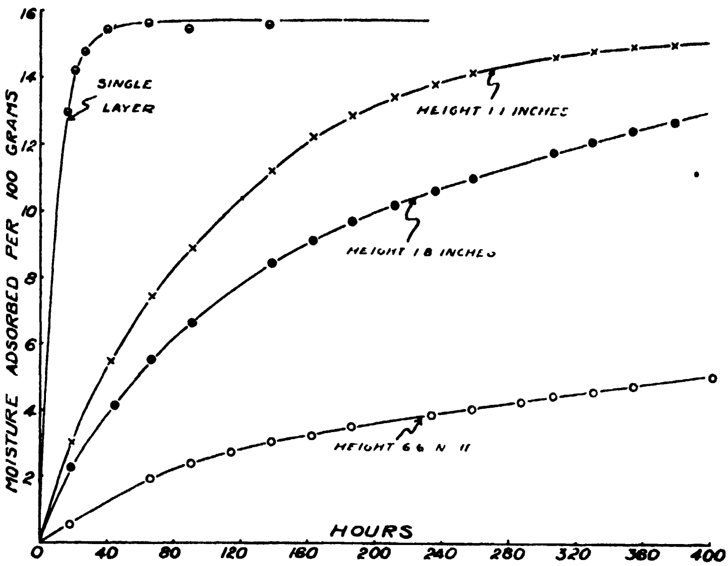

FIG. 13. *Effect of depth of wheat on rate of adsorption.*

These simple experiments give some idea of the length of time that is necessary before moisture from the atmosphere can penetrate into a mass of wheat. It is obvious that in any reasonable time only the surface layers of the wheat will be affected. Were this not so, wheat could not be stored so easily and conveniently in grain elevators. For there, wheat is left exposed at its upper surface to the atmosphere, and during the high humidity that prevails in the warm summer weather, the moisture content of the wheat would increase to a dangerous level were it not that the diffusion takes place so slowly. These results support the conclusions drawn from earlier experiments on the migration of moisture in a mass of wheat under a temperature gradient (1). The experiments also suggest that the time required for moisture to move from the surface of a kernel of wheat into the kernel is, under all ordinary conditions, but a small fraction of the time necessary for the vapor to diffuse up to the surface. In other words, it is the diffusion of water vapor through the air and through overlying layers of grain that limits the amount of moisture taken up by wheat rather than any resistance to moisture movement inherent in the grain itself. Cassie (3) has arrived at a similar conclusion for the change of moisture content of textile fibers. He finds that "the time of diffusion of water vapour from the surface to the interior of the fibre must be of little significance" in comparison with the time of diffusion of the water vapor up to the surface of the fiber. The wheat does, however, possess some quality that resists complete drying.

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DRIED WHOLE EGG POWDER

XXVIII. REPRODUCIBILITY AND INTERRELATION OF METHODS OF ASSESSING QUALITY[1]

By Jesse A. Pearce[2] and M. W. Thistle[2]

Abstract

The relation between palatability and fluorescence value, previously established for 33 samples of plain egg powder, was substantiated by comparisons for 118 samples. Fluorescence measurements were more readily reproduced among various laboratories than measurements of potassium chloride value. Batter density measurements were found to be a satisfactory measure of the baking quality of sugar–egg powder and were more convenient than the baking of test cakes. Particle size of spray-dried sugar–egg powder was also related to baking quality; powder falling between 50 and 200 mesh (U.S. Bureau of Standards) yielded the lightest sponge goods.

Introduction

During the course of work reported in earlier papers in this series, several tests of quality in plain dried egg powder were described and some of these have been written into standards governing quality (1, 2, 5). The reproducibility of these tests became the subject of collaborative studies. On sugar–egg powder, measurements of baking volume were inconvenient for control testing and simpler methods were sought. Some of these were also assessed in a collaborative study.

The present paper, describing the results of this work, is divided into two main parts. The first deals with studies on plain egg powder and describes further assessment of the fluorescence–palatability relation (7), and collaborative measurements of fluorescence (8) and potassium chloride values (11). The second deals with studies on sugar–egg powder; it describes the relations between a number of measurements and cake volume (6), and a collaborative study of foam density, batter density (5), and cake volume (5) as methods of assessing baking quality.

Plain Egg Powder

The Palatability–Fluorescence Relation

In the first report (7) on the relation between palatability scores and fluorescence value a correlation coefficient of −.90** was obtained for a 14-man panel testing 33 samples of dried egg. The equation relating these characteristics was

$$y = 2.32 - 0.12\,x,$$

where y is the logarithm of the photofluorometer reading and x is the palatability rating on a scale ranging from 10 for excellent to 0 for inedible samples.

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Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as paper No. 220 of the Canadian Committee on Food Preservation and as N.R.C. No. 1877.
[2] *Biochemist, Food Investigations.*
** *Exceeds the 1% level of statistical significance.*

In the present study, eating-quality assessments by a 12-man panel on 118 samples over a wide range of quality were found to be related to fluorescence values (8) by the equation

$$y = 2.28 - 0.11\, x$$

with a correlation coefficient of $-.84^{**}$. Neither of the parameters of this equation differed significantly from those previously established, and there was no significant difference between the two correlation coefficients.

Collaborative Study of Fluorescence and Potassium Chloride Values

To provide material for this study, a sample of good egg powder was thoroughly mixed, divided into four lots, treated as shown in Table I, canned in 100-gm. samples in No. 1 tins, and held at −40° F. Samples from each

TABLE I

FLUORESCENCE AND POTASSIUM CHLORIDE VALUES ON EGG POWDER OF FOUR QUALITY LEVELS

(Rounded averages of 24 determinations)

Sample designation	Treatment, days at 110° F.	Fluorescence value	Potassium chloride value
Good	None	22	71
	2	29	68
Poor	5	49	43
	9	68	34

treatment were distributed (by air express where necessary) under randomized code numbers, at monthly intervals for four months, to each of the three co-operating laboratories. Each laboratory determined the fluorescence (5) and potassium chloride values (5) on duplicate samples from each tin.

Since duplicate analyses on 'poor' quality powders were significantly more variable than those for 'good' quality powders, the data had to be divided for separate statistical analyses.

The fluorescence measurements made by Laboratory 2 on poor quality egg powders (Table II) were lower than the measurements made in the other two laboratories but, for good egg powders, there was no significant difference attributable to laboratories. The potassium chloride values determined in Laboratory 1, for both good and poor quality powders, were significantly lower than measurements made in either of the other two laboratories. Laboratory 3 consistently recorded high values for the 'good' sample with an average potassium chloride value of 68 (Table I).

An assessment based upon the differences between laboratories, within laboratories, between replicate samples, and between duplicate analyses is given in Table III. The average difference between any two fluorescence

** *Exceeds the 1% level of statistical significance.*

TABLE II

FLUORESCENCE AND POTASSIUM CHLORIDE DETERMINATIONS AT THREE LABORATORIES FOR 'GOOD' AND 'POOR' SAMPLES OF DRIED EGG POWDER

(Averages of 16 determinations)

Laboratories	Fluorescence		Potassium chloride	
	Good samples	Poor samples	Good samples	Poor samples
1	26.5	58.9	67.7	35.3
2	24.8	56.2	69.4	40.6
3	25 0	59.8	70.4	39.6
Necessary difference, 5% level of significance	—	2.7	1.4	2.3

TABLE III

ESTIMATED TOTAL ERRORS OF DETERMINATIONS OF FLUORESCENCE AND POTASSIUM CHLORIDE VALUES

(Based upon results from three laboratories)

Estimates of error	Fluorescence		Potassium chloride	
	Good samples	Poor samples	Good samples	Poor samples
Standard deviation of a single observation	1 6	3 0	2 0	3.5
Average difference between two observations selected at random	1 8	3 4	2.3	4.0
'Maximum' difference between two observations selected at random (5% point)	4 7	9 0	6 1	10.5

value determinations on a good egg powder, under the conditions of this experiment, was likely to be less than 2 units, and the 'maximum' difference (5% point) was likely to be less than 5 units. The corresponding figures for the potassium chloride determination were 2.5 and 6.5 units. Of the two methods of assessing egg powder quality, the fluorescence method was better than the potassium chloride method from the standpoint of reproducibility of results, since, in addition to random errors, determinations of the potassium chloride values were in error because of systematic differences between one laboratory and another.

Sugar-Egg Powder

Since sugar-egg powder is intended for use in baked goods, its baking quality must be controlled. But the baking of test cakes is often inconvenient, and a simpler method of measuring baking quality was desired.

Foaming volume measurements provided useful information in some of the initial experimental work (3), but it was observed that this measure was subject to irregularities (4), and it did not appear to be satisfactory for controlling commercial production.

In the present work, the relations between cake volume and a number of other characteristics were examined, with special attention to determinations of particle size. This was followed by a collaborative test of the cake volume methods in current use. Simple density measurements on cake batter had been suggested as a possible test of baking quality, and density measurements were therefore included in this collaborative study.

Relation Between Some Quality Tests and Cake Volume

The powder used in this part of the study was produced in two Canadian plants using cone-type driers during the fall of 1945: 22 samples were taken at various times from the main drying chamber of one plant and nine samples from the main chamber of the other. The samples were produced under a variety of conditions and represented the range of quality likely to be met in commercial operations.

The analytical measurements made on these powders included determinations of moisture content (11), fluorescence value (8), potassium chloride value (11), pH (5), foaming volume (4, 6, 9), foam stability (6), and cake volume (6). In addition, packing density was determined by measuring the volume occupied by 1 lb. of powder when poured into a container and subjected to three free falls of four inches. Finally, particle size determinations were made by sieving a 1 lb. sample on a Ro-tap shaker for one hour and determining the weight of powder in the various mesh ranges used (U.S. Bureau of Standards). Although this does not provide an exact separation of the powder (10), it was believed satisfactory for the present purpose.

Most of these tests were useless from the standpoint of prediction of cake volume because either the correlation coefficients were too low or different equations had to be used for powders from different plants. Foaming volume was again related to baking volume ($r = .73^{**}$). However, sieve analysis of powders as received from the driers provided the best estimate of cake volume ($R = .80^{**}$), a fact that seemed to warrant further work.

Relation Between Particle Size and Cake Volume

In a preliminary study, an attempt was made to assess the effect of various drying conditions on batches of spray-dried powder of uniform particle sizes, to be obtained by using a fixed nozzle aperture, but this failed because these other drying conditions also had an effect on particle diameter.

During the winter of 1946, cakes were baked using 30 samples of sugar–egg powder from the main drying chambers of eight plants and 14 samples from the secondary collectors of three plants. Samples of the same powders were

** *Exceeds the 1% level of statistical significance.*

sieved as previously described. The prediction equation for powders from the main chambers was:

$$y = 229.3 - 0.094x_1 + 0.556x_2 + 0.450x_3 + 0.453x_4 ,$$

where y is the cake volume in ml. and x_1, x_2, x_3, and x_4 are the percentages of the powder falling between mesh sizes 16 and 50, 50 and 80, 80 and 100, and 100 and 200 respectively. The same equation could be used for powders from the secondary collectors, except that the first term was reduced from 229.3 to 213.3; i.e., on the average, powders from the main chambers gave cakes 16 ml. larger than samples with the same sieve analysis from secondary collectors. However, for both equations, the correlation coefficient was only .75** and the standard error of estimate was ± 11.4 ml. This showed that sieve analysis alone was not a satisfactory measure for controlling the baking quality of commercially produced sugar-egg powders.

These equations indicated that attention should be given to adjusting the conditions of spray-drying to produce powders finer than 50 mesh. Optimum cake volume at 80 to 100 mesh was suggested by an earlier study (6). The poor baking quality of the largest particles may be due to the fact that they dry most slowly and deteriorate while they are wet.

Collaborative Study of Tests of Baking Quality

Since the foregoing work yielded no satisfactory substitute for cake volume measurements, it seemed advisable to examine the baking tests in current use, and coincidentally, to reassess the possibility of using foam density and to assess batter density for predicting baking quality.

For this study, 30 samples of spray-dried sugar–egg were drawn from Canadian commercial production during the summer of 1946: 20 samples were obtained from main drying chambers and 10 samples from secondary collectors. Each sample was thoroughly mixed in a mechanical device and aliquots were packed in No. 1 tins and sent to the participating laboratories for triplicate analyses. The procedure described elsewhere (5) for determining batter density and cake volume was used with minor modifications* by most of the laboratories. Laboratory 1 used a simpler procedure (6). Laboratory 5 used both procedures and their results for the simpler procedure are listed as Laboratory 5*A*. Foam density was determined on the batter before the addition of flour.

For powders from the main drying chambers, differences between samples were nearly all within the limits of experimental error and hence failed to provide any information on the interrelations under study. For secondary collector powders, the correlation coefficients were considerably higher and most of them were statistically significant (Tables IV and V).

* *The details, if desired, can be obtained by requesting a copy of Interim Report No. 46-12-1, Division of Applied Biology, National Research Laboratories, Sussex St., Ottawa.*

** *Exceeds the 1% level of statistical significance.*

TABLE IV

INTERRELATION BETWEEN THE METHODS USED BY FIVE LABORATORIES FOR ASSESSING THE BAKING QUALITY OF 10 SAMPLES (SECONDARY COLLECTOR) OF SUGAR–EGG POWDER

(Simple correlation coefficients between laboratories)

Methods	Lab. No. 2	Lab. No. 3	Lab. No. 4	Lab. No. 5	Lab. No. 5A
CAKE VOLUME					
Lab. No. 1	.81**	.92**	.88**	.82**	.71*
Lab. No. 2		.75*	.60	.59	.52
Lab. No. 3			.78**	.66*	.74*
Lab. No. 4				.89**	.75*
Lab. No. 5					.85**
FOAM DENSITY					
Lab. No. 1	.52	.87**	.75*	.79**	
Lab. No. 2		.51	.50	.63	
Lab. No. 3			.86**	.80**	
Lab. No. 4				.64*	
BATTER DENSITY					
Lab. No. 1	.59	.86**	.67*	.93**	
Lab. No. 2		.55	.61	.70*	
Lab. No. 3			.75*	.92**	
Lab. No. 4				.74*	

* *Attains 5% level of statistical significance.*
** *Attains 1% level of statistical significance.*

TABLE V

INTERRELATION BETWEEN THE METHODS USED FOR ASSESSING THE BAKING QUALITY OF 10 SAMPLES (SECONDARY COLLECTOR) OF SUGAR–EGG POWDER, AT EACH OF FIVE LABORATORIES

(Simple correlation coefficients between methods)

Laboratories	Cake volume × foam density	Foam density × batter density	Cake volume × batter density
1	−.88**	.99**	−.87**
2	−.61	.84**	−.87**
3	−.84**	.99**	−.85**
4	−.66*	.83**	−.79**
5	−.95**	.86**	−.88**
5A	−.79**	.86**	−.87**

* *Attains 5% point of statistical significance.*
** *Attains 1% point of statistical significance.*

Table V shows the interrelation, within laboratories, between the various methods of measuring baking quality. At some laboratories, correlation coefficients between cake volume and foam density were too low for prediction purposes. The relation between foam density and batter density is of little practical importance. However, the highly significant correlation coefficients for the relation between cake volume and batter density indicated that a batter density test might be useful for measuring baking quality. Calculations

showed that sugar–egg powder giving a batter with density greater than 0.43 by any of the procedures used was unsuitable for use in the best class of sponge goods. Therefore, during the past two years, a batter density test (5) has been used to control the baking quality of sugar–egg powder exported from Canada.

Acknowledgments

The laboratories of the following institutions collaborated with the National Research Laboratories, Ottawa, throughout this work: Borden's, New York; Canada Egg Products Limited, Saskatoon; Science Service and Experimental Farms Service of the Dominion Department of Agriculture, Ottawa; and Swift and Company, Chicago. Without their wholehearted co-operation these studies would not have been possible. We are particularly indebted to Dr. L. Mink of Swift and Company, Chicago, who made the original suggestion that measurements of batter density might be useful in predicting the baking quality of sugar–egg powder.

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A NICKEL-ALUMINUM-MOLYBDENUM CREEP RESISTANT ALLOY[1]

By H. V. Kinsey[2] and M. T. Stewart[3]

Abstract

This paper describes a preliminary study of alloys of nickel and aluminum modified with molybdenum. The purpose of this work is to develop an alloy for use under conditions of stress at temperatures of 815° C. (1500° F.) and over. The room temperature mechanical properties of alloys of nickel and aluminum, and the influence of molybdenum on these properties, have been investigated. Certain combinations of nickel, aluminum, and molybdenum have been shown to possess tensile strengths well over 100,000 lb. per sq. in. at room temperature, and it has been demonstrated that certain characteristic microstructures, dependent upon the ratio of nickel to aluminum, are essential for the realization of these high strengths. Creep-rupture tests at 815° C. (1500° F.) have been carried out on typical nickel–aluminum–molybdenum alloys. The results have shown that certain of these alloys are superior in many respects to existing high temperature alloys, when tested under creep-rupture conditions at 815° C. (1500° F.). The same characteristics of microstructure that are essential for high room temperature strengths were also found to be necessary to obtain good creep-rupture characteristics at 815° C. (1500° F.).

Introduction

So much has been written on the subject of alloys for use in gas turbine blades that the more important requirements for such materials are now widely recognized. They must have chemical stability to ensure resistance to corrosion by hot combustion gases. A second requirement is stability of microstructure at anticipated operating temperatures, to minimize the deterioration of mechanical properties during long exposure to elevated temperatures. Also, a high strength–weight ratio is desirable in alloys under consideration for gas turbine blades, since the stress causing creep in these parts is generated by centrifugal force.

The high melting points and relatively low densities of the nickel-rich nickel–aluminum alloys, specifically of the intermetallic compound NiAl, suggested that an investigation of the creep properties of alloys based on the nickel–aluminum system might be worth while. The nickel aluminum phase diagram (1) is presented in Figs. 1 and 2.

All the alloys to be dealt with in this paper were melted by high frequency induction in magnesia crucibles. Test bars were centrifugally cast into molds produced by the "lost wax" precision casting technique.

All room temperature tensile tests were made on the Hounsfield tensometer, using the test-bar design shown in Fig. 3. All creep and stress-rupture tests

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[2] *Metallurgical Engineer; Head, High Temperature Metals Laboratory, Physical Metallurgy Research Laboratories, Division of Mineral Dressing and Metallurgy, Bureau of Mines, Ottawa.*

[3] *Junior Research Officer, Associate Committee on High Temperature Metals, National Research Council of Canada, Ottawa, Canada.*

were obtained with the test bar design shown in Fig. 4. Note that one end of this bar is hollow, to promote directional solidification.

The metal temperatures of the melts cast into the large test bars (see Fig. 4) were measured with an immersion platinum–rhodium thermocouple used in conjunction with a high speed potentiometer-type temperature recorder.

The metals used in this work are listed in Table I, together with the analyses obtained from the suppliers.

TABLE I

COMPOSITIONS OF MATERIALS USED

Material	Chemical analysis, %
Nickel (electrolytic)	Ni, 99.9
Cobalt (electrolytic)	Co, 99 5. Major impurity: Cu.
Aluminum	Al, 99.5. Impurities: Fe, Mn, Si.
Molybdenum	Mo, 99.5. Impurities: Mn, Si, Fe.

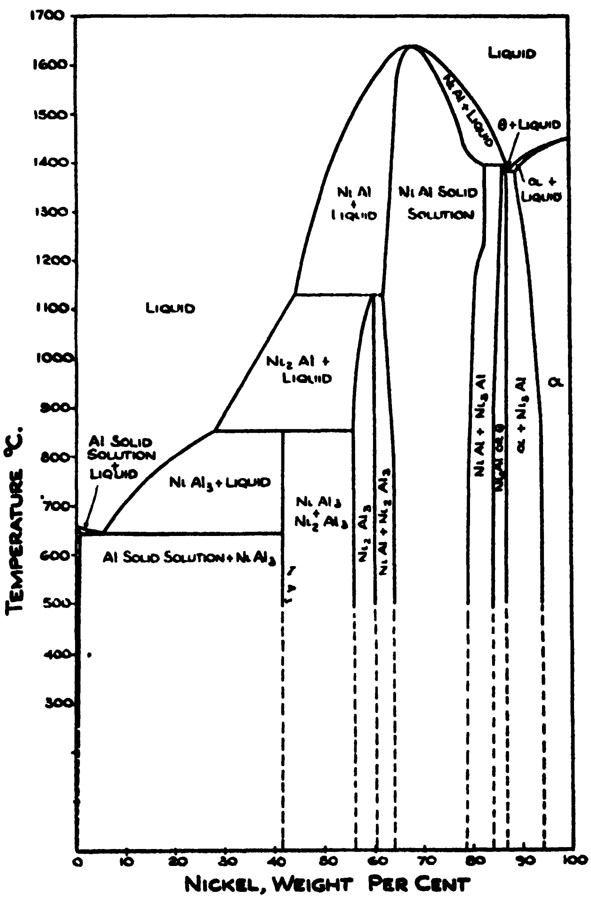


FIG. 1. *Nickel–aluminum phase diagram over complete range.* (*After Alexander and Vaughan* (*1*).)

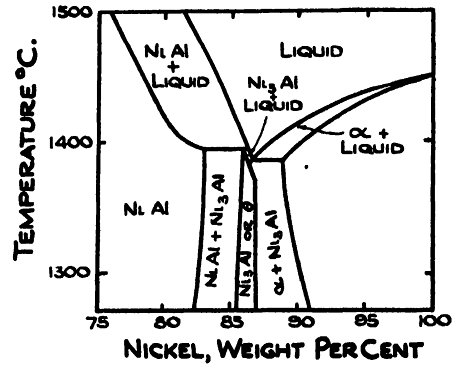


FIG. 2. *Nickel–aluminum phase diagram for the range of 75 to 100% nickel. (After Alexander and Vaughan (1).)*

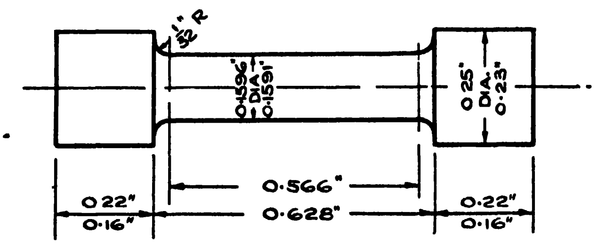


FIG. 3. *Tensile bar for Hounsfield tensometer.*

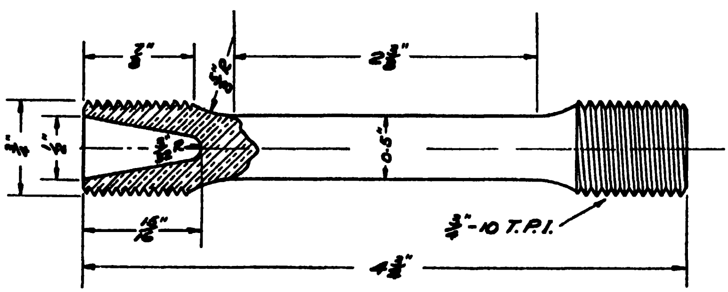


FIG. 4. *Precision cast ½ in. diameter creep test bar.*

System of Alloy Nomenclature

With the exception of the preliminary group of four binary alloys of nickel and aluminum, all the alloys to be discussed were made up of nickel, aluminum, and molybdenum. In order to facilitate the discussion of these alloys, the following nomenclature was devised.

If the Ni : Al ratio and the amount of molybdenum present are stated, then the alloy is fully described. For example, let the Ni : Al ratio be 10.3 : 1 and the amount of molybdenum present be 14.7%. Then the alloy is identified by the expression 103M147. The letter "M" is included to indicate that the third element present is molybdenum. If the Ni : Al ratio is 7.6 : 1 and the molybdenum content is 8.2%, then the expression 76M82 identifies the alloy.

Nickel–Aluminum Alloys

Table II lists the phase zone boundary limits in the nickel-rich portion of the nickel–aluminum phase diagram (see Figs. 1 and 2). These boundary limits are stated in terms of the ratio of nickel to aluminum.

TABLE II

PHASE ZONE BOUNDARY LIMITS BELOW 950° C. (1742° F.) IN THE NICKEL–ALUMINUM SYSTEM

Ni : Al ratio	Phases present
2.3 : 1 to 3.76 : 1	NiAl solid solution
3.76 : 1 to 5.25 : 1	NiAl + Ni_3Al
5.25 : 1 to 6.7 : 1	Ni_3Al
6.7 : 1 to 15.6 : 1	Ni_3Al + alpha solid solution
Over 15.6 : 1	Alpha solid solution

Four binary alloys of nickel and aluminum, characteristic of the first four phase zones listed in Table II, were chosen as a starting point for this work. These alloys are listed in Table III.

TABLE III

BINARY NICKEL–ALUMINUM ALLOYS

Alloy No.	Chemical analysis, %		Ni : Al ratio		Anticipated phases
	Nickel	Aluminum	Sought	Obtained	
1	73.08	26.92	3 : 1	2.7 : 1	NiAl
2	83.19	16 81	4 : 1	4.9 : 1	NiAl + Ni_3Al
3	84.70	15 30	5.6 : 1	5 6 : 1	Ni_3Al
4	92.2	7.8	9 : 1	11 8 : 1	Ni_3Al + alpha solid solution

Hounsfield tensometer test bars were cast and the room temperature mechanical properties given in Table IV were determined.

TABLE IV

ROOM TEMPERATURE MECHANICAL PROPERTIES OF NICKEL–ALUMINUM ALLOYS

Alloy No.	Tensile strength, p.s.i.		Average elongation, %	Vickers hardness value (30 kgm. load)
	Average	Maximum		
1	Nil	Nil	Nil	389
2	28,500	30,000	"	404
3	60,000	62,000	"	265
4	64,667	77,000	18.3	346

The properties listed in Table IV are shown plotted against the Ni : Al ratio in Fig. 5. It will be noted that Alloys 3 and 4 above, which on the basis of their Ni : Al ratio would not be expected to show any of the NiAl constituent, possess the most promising room temperature mechanical properties.

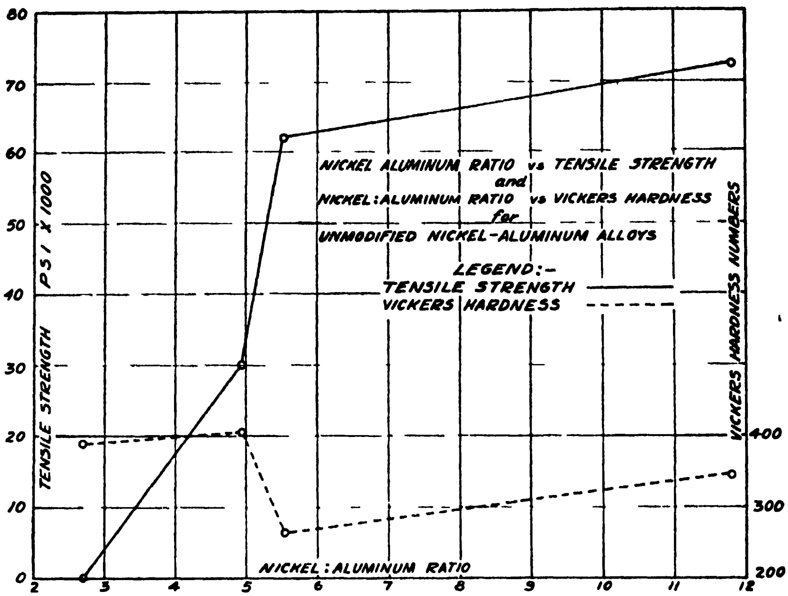


FIG. 5. *Mechanical properties vs. Ni : Al ratio.*

Metallography of Nickel–Aluminum Alloys

Figs. 6 to 11, inclusive, are photomicrographs showing the microstructure of Alloys 1, 2, 3, and 4, respectively. Alloy 1, with a Ni : Al ratio of 2.7 : 1, has only one phase, as would be expected. Alloys 2 and 3 have two phases. Alloy 2 has a Ni : Al ratio of 4.9 : 1, which indicates the presence of both NiAl and Ni_3Al. Alloy 3 has a Ni : Al ratio of 5.6 : 1. Under equilibrium conditions this alloy should consist structurally of a single phase, Ni_3Al. However, since all the microstructures under consideration are of "as cast" alloys, the presence of two phases in Alloy 3 is not surprising. These two phases would be expected to be NiAl and Ni_3Al.

FIG. 6. *Alloy No. 1, as cast. Electrolytic polish, Vilella's etchant. ×200. Ni, 73.08%; Al, 26.92%.*

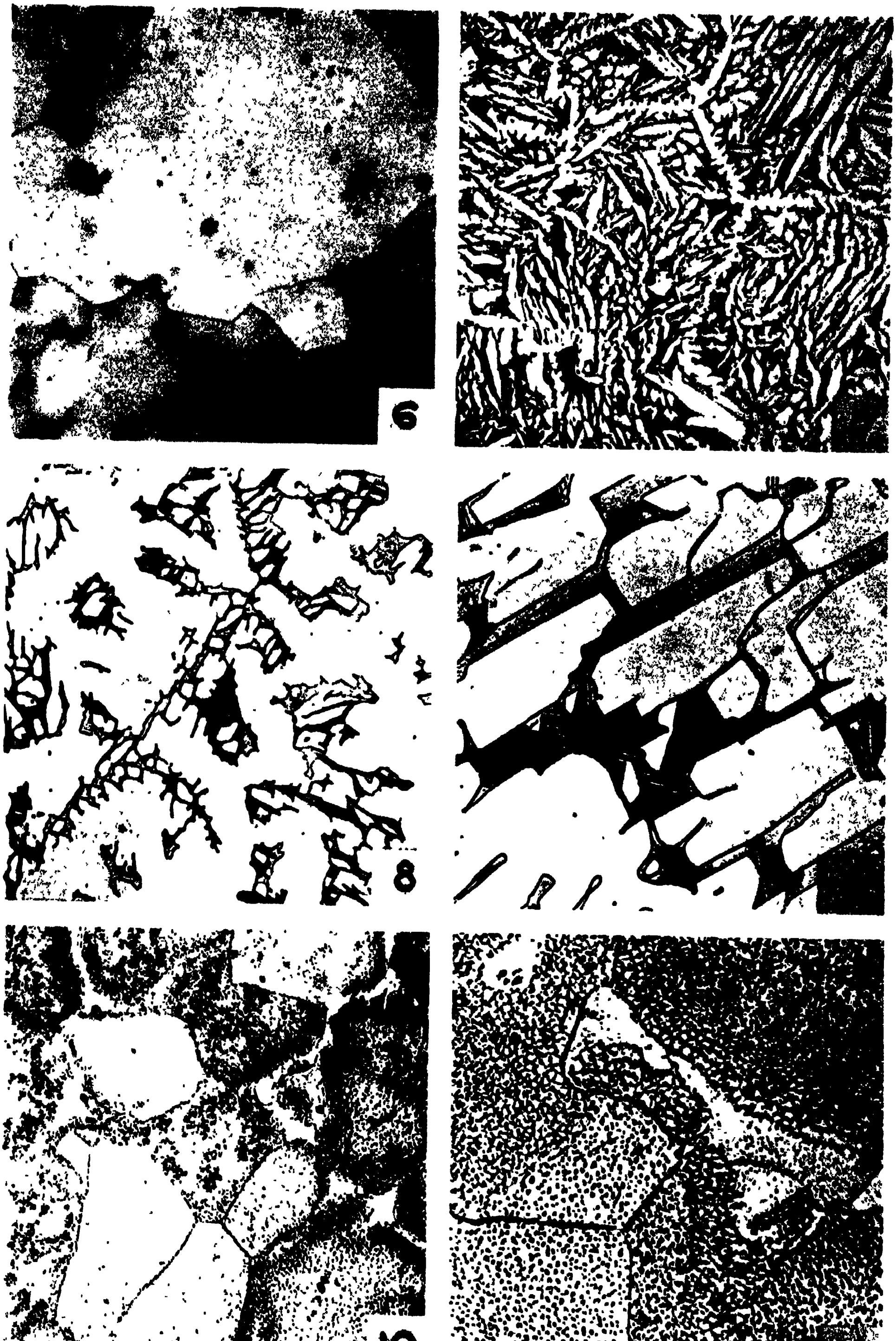
FIG. 7. *Alloy No. 2, as cast. Mechanical polish, Vilella's etchant. ×200. Ni, 83.19%; Al, 16.81%.*

FIG. 8. *Alloy No. 3, as cast. Mechanical polish, Vilella's etchant. ×200. Ni, 84.70%; Al, 15.30%.*

FIG. 9. *Same as Fig. 8. ×750.*

FIG. 10. *Alloy No. 4, as cast. Mechanical polish; etchant, ferric chloride plus hydrochloric acid in alcohol. ×200. Ni, 92.2%; Al, 7.8%.*

FIG. 11. *Same as Fig. 10. ×750.*


6
8
10

A comparison of the microstructures of Alloys 2 and 3, as shown in Figs. 7 and 8, will enable us to establish the identity of these two phases. There is a dark-etching phase and a light-etching phase present. Alloy 2, which has a lower Ni : Al ratio than Alloy 3, should be expected to have more of the NiAl phase than Alloy 3. Since there is more of the dark-etching phase in Alloy 2 than in Alloy 3, it is assumed that this dark-etching phase in these structures is NiAl and the light-etching phase is Ni_3Al.

The Ni : Al ratio of Alloy 4 indicates that it will consist structurally of two phases, alpha and Ni_3Al. Its microstructure, as shown in Figs. 10 and 11, indicates the presence of two phases. Most of the structure is characteristic of the structure obtained when a secondary phase precipitates from a primary solid solution owing to a shift in solubility with falling temperature. From the position of this alloy in the nickel–aluminum system, it would be expected to freeze out largely as alpha solid solution and to precipitate Ni_3Al on cooling below 1200° C. It is apparent, then, that the precipitated phase in this alloy is Ni_3Al and that the matrix is alpha solid solution.

Attention is drawn to the clear white areas visible in Fig. 10. According to Alexander and Vaughan (1), these are areas of Ni_3Al that, on freezing, were the alpha-Ni_3Al eutectic. They have shown that this eutectic cannot exist below 1370° C., owing to the increase of solubility of nickel in Ni_3Al that occurs between 1385° C. and 1370° C., which results in the disappearance of what little alpha has separated in the eutectic. The fact that some eutectic formed in Alloy 4 may be explained by the fact that sufficient segregation occurred during freezing to permit this formation.

Nickel-Aluminum-Molybdenum Alloys

The fact that molybdenum is a vital constituent of many high temperature alloys prompted a decision to investigate its influence on nickel–aluminum alloys. The program adopted involved preliminary tests at room temperature, to be followed by creep and creep rupture tests on such alloys as proved castable and displayed promise from consideration of their room temperature properties.

For a preliminary study of room temperature properties, these molybdenum-modified alloys were divided into four groups, each group having a constant Ni : Al ratio, so that, in effect, an attempt was made to study the influence of various molybdenum additions to the alloys listed in Table III. Alloys 1, 3, and 4 of Table III were the starting point for three of these groups. The fourth group was based on a Ni : Al ratio of 19 : 1, which represents a single-phase alpha solid solution alloy.

These alloys are listed in Table V. Fig. 12 shows the position of these alloys on the ternary nickel–aluminum–molybdenum triangle. This chart also contains the nickel–aluminum phase diagram (1) and the nickel–molybdenum phase diagram (2).

TABLE V

CHEMICAL ANALYSES OF NICKEL-ALUMINUM-MOLYBDENUM ALLOYS OBTAINED

Alloy sought	Alloy obtained	Chemical analysis, %		
		Nickel	Aluminum	Molybdenum
30M44	30M47	71.24	23.73	4.72
30M162	30M149	63.80	21.24	14.91
30M250	35M202	61.90	17.90	20.2
30M350	30M247	56.65	18.70	24.65
30M450	29M386	45.55	15.83	38.62
30M550	28M511	35.95	12.95	51.10
57M50	54M39	81.02	15.04	3.94
57M100	57M106	76.04	13.36	10.60
57M150	55M156	71.36	13.07	15.57
57M250	57M131	74.0	12.9	13.10
57M350	59M320	58.2	9.8	32.0
57M450	57M384	52.4	9.2	38.4
57M550	56M443	47.3	8.4	44.3
90M50	90M53	85.25	9.48	5.27
90M100	86M104	80.2	9.37	10.43
90M150	130M177	76.5	5.83	17.67
90M250	94M248	68.0	7.20	24.80
90M350	89M357	57.8	6.5	35.7
190M50	177M46	90.5	4.95	4.55
190M100	165M105	84.4	5.10	10.50
190M150	172M161	79.3	4.6	16.1
190M250	185M255	70.7	3.8	25.5

Room Temperature Mechanical Properties of Nickel-Aluminum-Molybdenum Alloys

Three bars from each of the alloy heats listed in Table V were pulled in room temperature tensile tests. The results are listed in Table VI. Vickers hardness values are also recorded in this table.

The results of these tensile tests are summarized graphically in Fig. 13, which shows the influence of molybdenum on the tensile strength and hardness of alloys of several nickel-aluminum ratios. Evidently molybdenum is most effective as a strengthener when nickel and aluminum are in such a ratio that a binary alloy of nickel and aluminum would consist structurally of Ni_3Al + alpha solid solution, or alpha solid solution alone (see Fig. 1).

Metallography of Nickel-Aluminum-Molybdenum Alloys

Figs. 14 to 21 illustrate the significant metallographic features of the alloys having the chemical and mechanical properties listed in Tables V and VI respectively.

These photomicrographs should be interpreted with reference to the phase zone boundary limits set out in Table II.

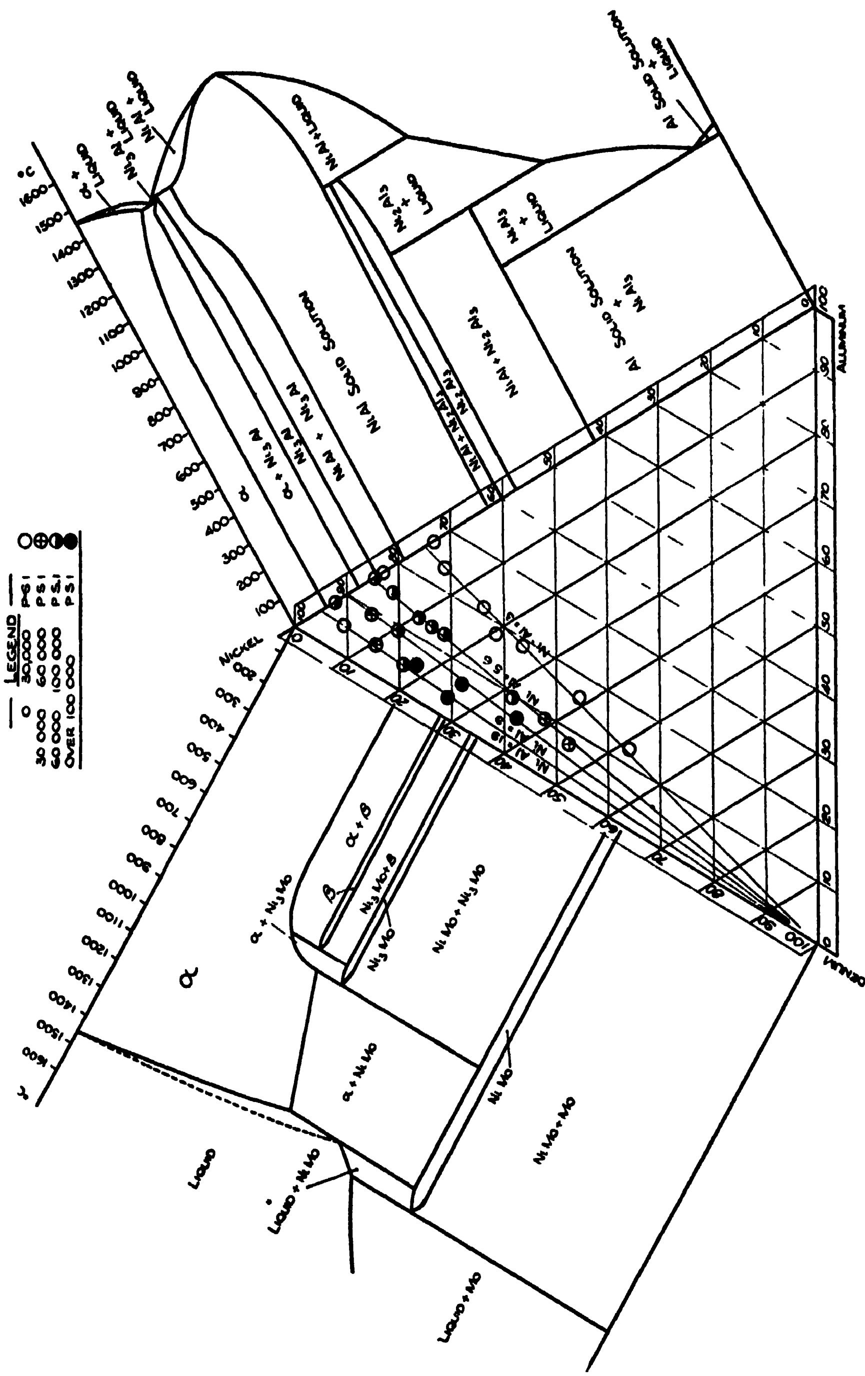


CHART SHOWING BINARY NICKEL-MOLYBDENUM AND NICKEL-ALUMINUM PHASE DIAGRAMS AND THE POSITION OF THE ALLOYS MADE IN THE NICKEL-ALUMINUM-MOLYBDENUM SYSTEM

TABLE VI

ROOM TEMPERATURE MECHANICAL PROPERTIES FOR NICKEL–ALUMINUM–MOLYBDENUM ALLOYS

Alloy	Tensile strength, p.s.i.		Average elongation, %	Vickers hardness value (30 kgm. load)
	Average	Maximum		
30M47	4,000	4,000	Nil	473
30M149	5,500	7,000	"	488
35M202	14,500	15,000	"	412
30M247	17,700	22,000	"	422
29M386	18,667	25,000	"	453
28M511	21,000	23,000	"	481
54M39	64,000	65,000	"	305
57M106	81,000	90,000	"	411
55M156	68,500	70,000	"	377
57M131	73,667	82,000	"	387
59M320	62,000	64,000	"	390
57M384	44,333	59,000	"	400
56M443	42,667	49,000	"	402
90M53	51,000	57,000	"	215
86M104	80,000	83,000	7 0	253
130M177	132,333	140,000	10 7	437
94M248	131,000	136,000	Nil	406
89M357	105,000	107,000	"	413
177M46	16,000	17,000	"	94 1
165M105	35,000	37,000	"	231
172M161	71,000	77,000	16 0	236
185M255	130,000	130,000	5 5	391

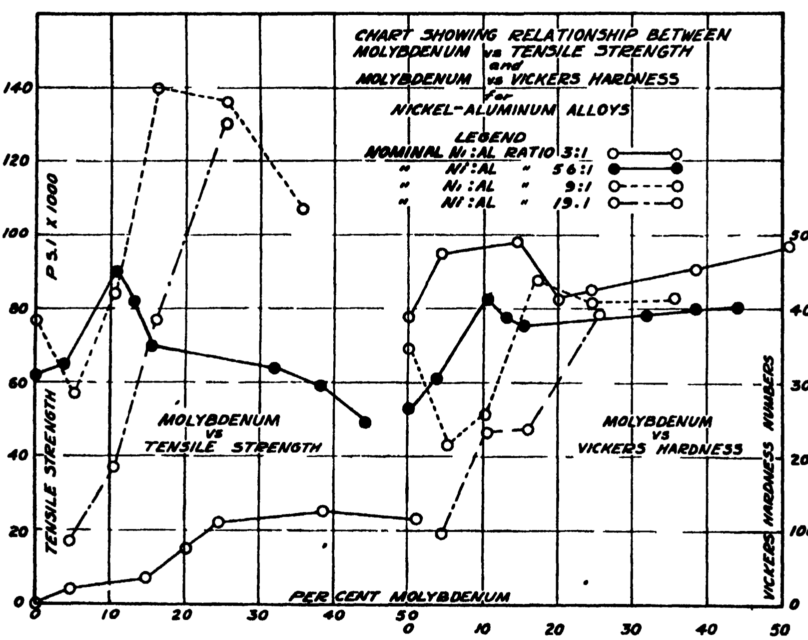
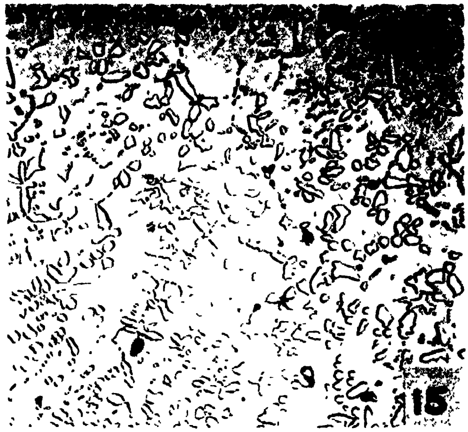


FIG. 13. *Mechanical properties of Ni-Al-Mo alloys.*



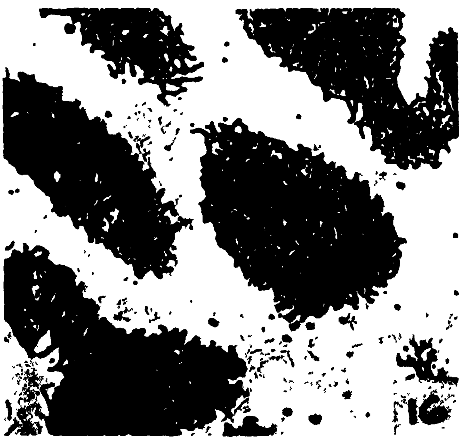
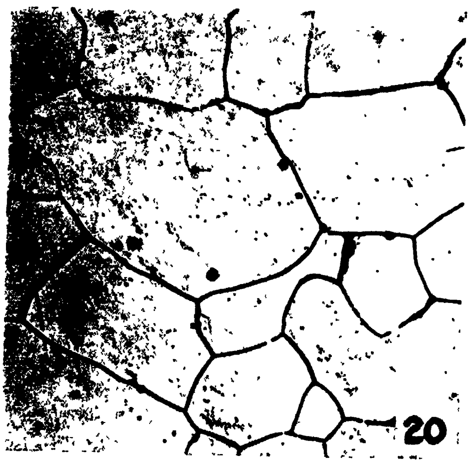


FIG. 14. *Alloy 30M149, as cast. Mechanical polish, Vilella's etchant.* ×*200. Ni, 63.8%; Al, 21.24%; Mo, 14.91%.*

FIG. 15. *Alloy 30M247, as cast. Mechanical polish, Vilella's etchant.* ×*200, Ni, 56.65%; Al, 18.70%; Mo, 24.65%.*

FIG. 16. *Alloy 57M106, as cast. Mechanical polish, Vilella's etchant.* ×*750. Ni, 76.04%; Al, 13.36%; Mo, 10.60%.*

FIG. 17. *Alloy 55M156, as cast. Mechanical polish, Vilella's etchant.* ×*750. Ni, 71.36%; Al, 13.07%; Mo, 15.57%.*



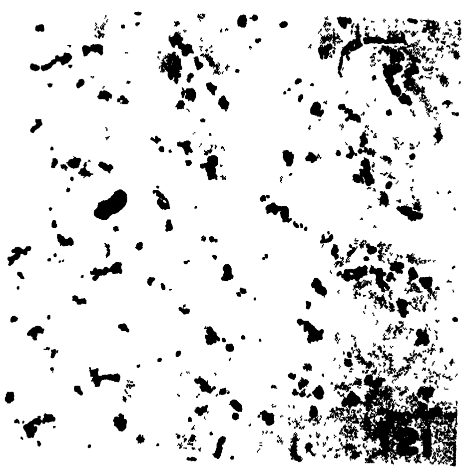


FIG. 18. *Alloy 94M248, as cast. Mechanical polish, Vilella's etchant. ×200. Ni, 68%; Al, 7.20%; Mo, 24.8%.*

FIG. 19. *Alloy 89M357, as cast. Mechanical polish, Vilella's etchant. ×200. Ni, 57.8%; Al, 6.5% Mo, 35.7%.*

FIG. 20. *Alloy 165M105, as cast. Mechanical polish; etchant, ferric chloride plus hydrochloric acid in alcohol. ×200. Ni, 84.4%; Al, 5.1%; Mo, 10.5%.*

FIG. 21. *Alloy 185M255, as cast. Mechanical polish; etchant, ferric chloride plus hydrochloric acid in alcohol. ×200. Ni, 70.7%; Al, 3.8%; Mo, 25.5%.*

When the Ni : Al ratio is 3 : 1, the alloy may be expected to be basically NiAl. The addition of molybdenum to such an alloy causes the formation of a second phase. This is shown in Figs. 14 and 15, which are the microstructures of Alloys 30M149 and 30M247 respectively.

In as-cast binary nickel–aluminum alloys with a Ni : Al ratio of 5.7 : 1, previous work has shown that two phases, namely NiAl and Ni_3Al, may be present. These phases have been tentatively identified in Figs. 7 and 8. Based on this identification, it may be assumed that the dark-etching phase in the nickel–aluminum-molybdenum alloys having a Ni : Al ratio of 5.7 : 1 will be NiAl. The structures of typical alloys of this group, Alloys 57M106 and 55M156, are shown in Figs. 16 and 17.

The eutectic appearing in Alloys 57M106 and 55M156 is characteristic of the presence of molybdenum. This eutectic can be caused to disappear from Alloy 57M106 by heating to 1000° C. (1832° F.). It is therefore assumed that the presence of this eutectic in Alloy 57M106 in the as-cast condition is due to segregation on freezing, and that under conditions approaching equilibrium it will not occur in this alloy.

In alloys of the 9 : 1 Ni : Al ratio group, molybdenum again causes the occurrence of a characteristic phase. This is illustrated by Fig. 18, which is the microstructure of Alloy 94M248. (The NiAl phase is absent from this group of alloys.) As the molybdenum content increases, this phase becomes more massive, as is shown by Fig. 19, which is the microstructure of Alloy 89M357.

Alloys having a Ni : Al ratio greater than 15 : 1 are structurally single-phase alpha solid solution up to at least 16% Mo; Fig. 20 is characteristic of this microstructure. At 25% Mo a second phase appears; this may be seen in Fig. 21.

An attempt has been made tentatively to establish the identity of the phase that is associated with the presence of molybdenum. This identification is based on the work of Ellinger (2).

It would appear that this phase, which occurs as a eutectic in Alloys 57M106, 55M156, 94M248, and 89M357 (Figs. 16, 17, 18, and 19), and in a primary form in Alloys 30M149, 30M247 and 89M357 (Figs. 14, 15, and 20), could be the delta (NiMo) phase of the nickel–molybdenum system.

On this basis, Alloys 30M149, 30M247, and 89M357 are all hypereutectic with respect to molybdenum, since primary NiMo is present. The absence of primary NiMo in Alloys 57M106, 55M156, and 94M248 would indicate that these alloys are hypoeutectic with respect to molybdenum.

Summary of Metallographic Features

1. The addition of molybdenum to alloys of nickel and aluminum causes the appearance of a characteristic phase tentatively identified as NiMo. This phase will occur in the primary form when the alloy is hypereutectic with respect to molybdenum and it will occur in the eutectic form when the alloy is hypoeutectic with respect to molybdenum.

2. The limiting molybdenum content at which the phase NiMo will occur varies with the nickel : aluminum ratio.

3. The NiAl phase persists in the ternary alloys of nickel, aluminum, and molybdenum at nickel : aluminum ratios generally similar to those in the binary nickel–aluminum alloys.

4. The presence of the NiAl phase has a marked weakening effect on the alloy and renders it less responsive to strengthening by additions of molybdenum.

Creep-rupture Properties of Some Nickel–Aluminum–Molybdenum Alloys at 815° C. (1500° F.)

The alloys selected for creep-rupture tests are listed in Table VII. This choice was dictated by the wish to include a representative alloy of each of the groups shown in Table V. The molybdenum contents were chosen from consideration of the room temperature properties presented in Table VI. The cast test bars were of the design shown in Fig. 4.

TABLE VII

ALLOYS SELECTED FOR CREEP-RUPTURE STUDIES

Alloy	Chemical analysis, %		
	Nickel	Aluminum	Molybdenum
30M250	56	19	25
56M100	76	15	10
90M150	76	9	15
90M200	72	8	20
190M250	71	4	25

The liquidus and solidus temperatures of these alloys were first measured as an aid in determining the proper casting temperature. Both the freezing curve technique, employing an immersion platinum–rhodium thermocouple, and the metallographic method were employed. Table VIII lists the results of these measurements.

TABLE VIII

LIQUIDUS AND SOLIDUS TEMPERATURES

Alloy	Chemical analysis, %			Freezing curve data		Metallographic data
	Ni	Al	Mo	Liquidus, °C.	Solidus, °C.	Solidus, °C.
35M246	58.6	16.6	24.6	1625	1540	Not determined
76M151	75.6	16.9	15.1	1415	1290	" "
95M138	79.0	8.3	13.8	1370	1360	1325 – 1340
106M217	72.9	6.9	21.7	1360	1290	1285 – 1300
213M257	72.4	3.4	25.7	1375	1270	Not determined

On the basis of the data listed in Table VIII, a casting temperature of 1650° C. (3002° F.) was chosen for all alloys but 30M250, for which a casting temperature of 1750° C. (3182° F.) was used. The temperature of the test-bar molds was held within the range of 649° to 677° C. (1200° to 1250° F.).

All test bars cast were subjected to X-ray inspection as a final check on soundness. It was not possible to produce good test bars from Alloy 30M250. Two heats were attempted. All bars of Alloy 30M250 produced contained shrinks and hot tears. This alloy was therefore eliminated at this point.

The chemical analysis of the alloy heats that produced good test bars are listed in Table IX.

TABLE IX

CHEMICAL ANALYSIS OF ALLOYS PRODUCING RADIOGRAPHICALLY SOUND TEST BARS

Alloy	Chemical analysis, %				
	Ni	Al	Mo	Fe	Si
53M104	74.9	14.2	10.4	0.1	0.37
90M158	75.6	8.4	15.8	0.4	0.24
95M255	66.5	7.0	25.5	0.8	0.16
258M252	72.4	2.8	25.2	0.06	0.25

All but two of the creep-rupture tests were carried out at 815° C. (1500° F.). The results of these tests are summarized in Table X. The elongation vs. time curves for Alloys 90M158 and 95M255 are presented in Figs. 22 and 23.

TABLE X

SUMMARY OF CREEP-RUPTURE TESTS AT 815° C. (1500° F.)

Alloy	Stress, p.s.i.	Elongation on application of load, %	Hours to rupture	Total elongation, %	Minimum creep rate, % per hr.	Remarks
53M104	29,948	0.82	1	11		
	20 030	0.31	6	12½		
90M158	35,000	—	112	0 5	—	Extensometers not functioning
	29,945	0.15	285	2	0.0018	
	27,440	0.11	664	2.5	0.0015	
95M255	40,000	0.278	100	4.5	0.033	
	35,000	—	352	6	—	Extensometers not functioning
	35,000	0.25	236	6	0.012	See note below*
	30,000	0.18	556	4	0.0027	
	27,600	0.21	913	3	0.0022	
258M252	25,000	0.15	75	—	—	
	22,500	0.12	117	1.5	—	
	13,500	—	442	—	—	Extensometers not functioning
95M255	15,000	Test temperature, 982° C. (1800° F.). Adapter bar broke in seven hours. Elong. 1½%*				

* NOTE: *After being stressed to 15,000 p.s.i. at 982° C. for seven hours, this bar was used for a test at 815° C. with a stress of 35,000 p.s.i. Between these tests the bar was unstressed and cooled to room temperature.*

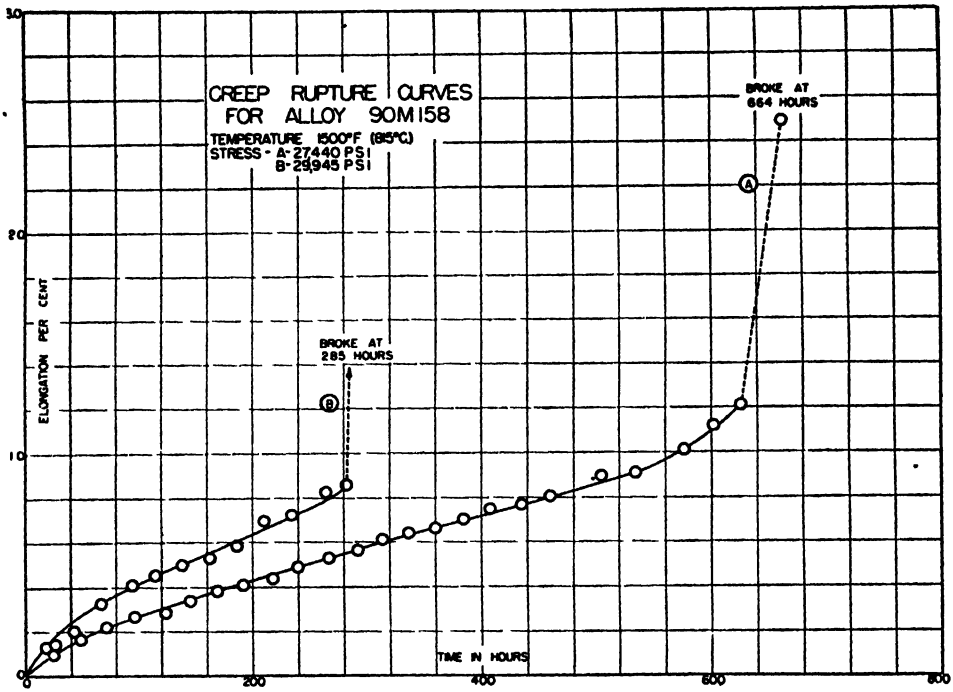


FIG. 22. *Creep-rupture curves, Alloy No. 90M158 at 815° C. (1500° F.).*

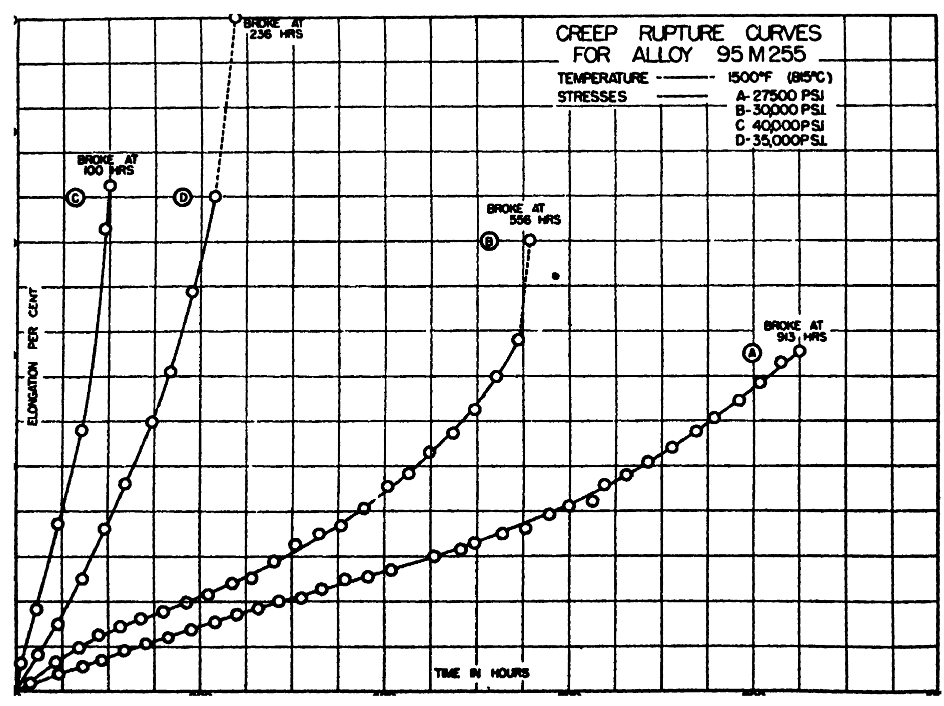


FIG. 23. *Creep-rupture curves, Alloy No. 95M255 at 815 ° C. (1500 ° F.).*

In certain tests, as noted in Table X, the extensometers were not functioning properly, and therefore no creep data are available from these tests.

It will be noted that one test is reported on Alloy 95M255 at 982° C. (1800° F.), using a stress of 15,000 p.s.i. This test lasted for seven hours before the adapter bar broke, at which time the test bar had elongated $1\frac{1}{2}\%$. This test bar was later put into test at 815° C. (1500° F.) under a stress of 35,000 p.s.i. It lasted for 236 hr. as compared to the 352 hr. of a duplicate bar that had been tested in the as-cast condition at 815° C. (1500° F.) using a stress of 35,000 p.s.i. All creep data for 35,000 p.s.i. at 815° C. (1500° F.) for Alloy 95M255 were obtained from the bar that was first tested at 982° C. (1800° F.) and subsequently tested at 815° C. (1500° F.).

The graphs shown in Figs. 24 and 25 summarize the results of the creep-rupture tests on Alloys 90M158 and 95M255 and compare these alloys with some of the existing standard and improved high temperature alloys. The chemical analyses of the alloys used for comparison purposes are listed in Table XI. These alloys are: a standard vitallium alloy, 30V-2(4); two modified vitallium alloys, 73J(4), and X-63(3); and alloys S-816 and Inconel "X".

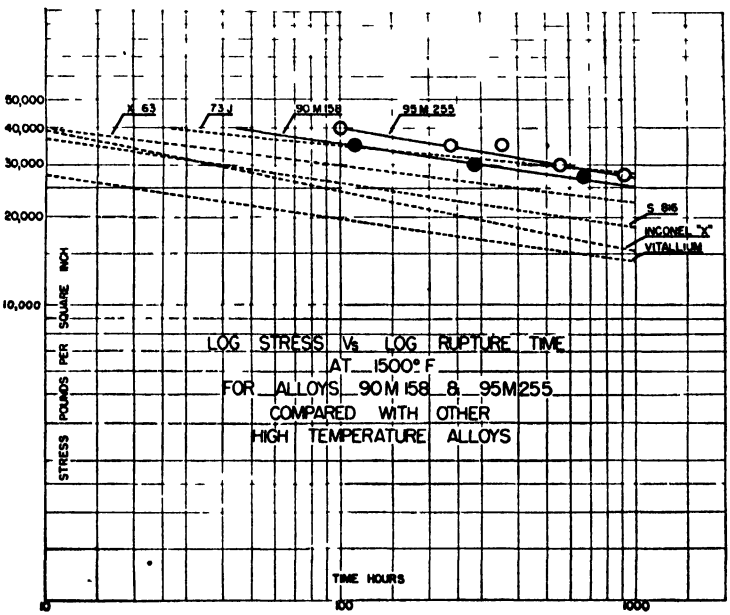


FIG. 24. *Graphical summary of creep-rupture tests at 815° C. (1500° F.) on alloys 90M158 and 95M255, and comparison with other high temperature alloys.*

Fig. 24 is a graph of log stress vs. log rupture time. Fig. 25 contains two graphs, one showing log stress vs. log time to 0.5% total creep strain, and the other showing log stress vs. log minimum creep rate.

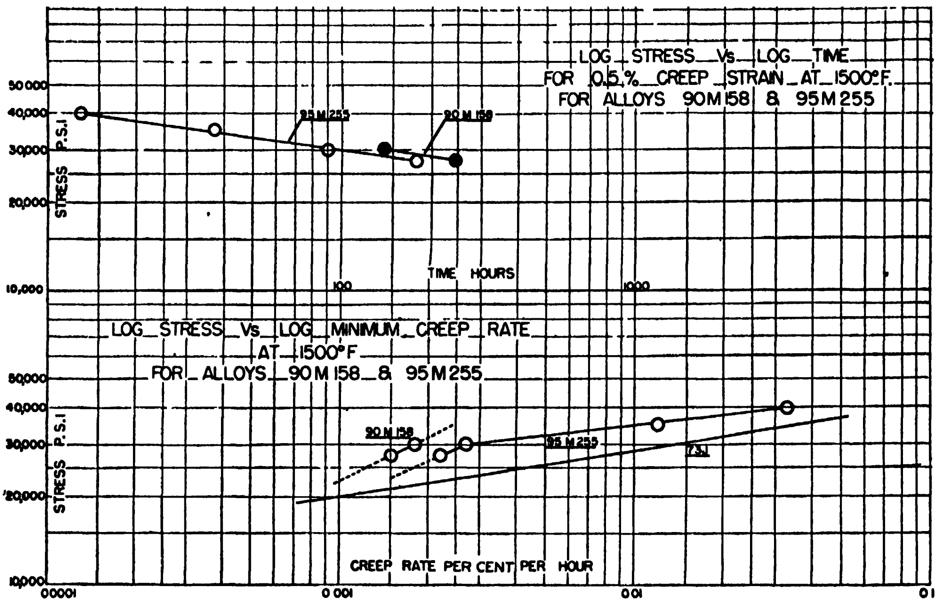


FIG. 25. *Creep-rupture results and comparisons at 815° C. (1500° F.).*

As a further basis of comparison, it is interesting to consider specific gravity values of existing alloys and of Alloys 90M158 and 95M255. These data are included in Table XI.

TABLE XI

CHEMICAL ANALYSES AND SPECIFIC GRAVITY OF COMPARATIVE ALLOYS

Element	Cast vitallium type			Wrought		90M158	95M255
	73J	X-63	30V-2	S-816	Inconel "X"		
	%						
Cobalt	60	57.5	69	43			
Nickel	6	10		20	73	75.6	66.5
Chromium	23	25	23	20	15		
Molybdenum	6	6	6	4		15.8	25.5
Tantalum	2						
Columbium				3.5	1		
Tungsten				4.5			
Titanium					2.5		
Aluminum					0.7	8.4	7.0
Iron				4 max.	7	0.4	0.8
Manganese		0.5		1.5	0.5		
Silicon		0.5		0.5	0.4	0.24	0.16
Carbon	0.75	0.5	0.3	0.35	0.04		
Specific gravity	*	*	8.30	8.66	8.3	7.6	8.0

* *Not available.*

The data presented in Table XII indicate for the various alloys the stress to cause both rupture and 0.5% total creep strain in 100, 1000, and 5000 hr. In Table XIII the data are arranged on a basis of minimum creep rate.

TABLE XII

CREEP-RUPTURE DATA AT 815° C. (1500° F.), SUMMARIZED ON A TIME BASIS

Alloy	100 Hr.				1000 Hr.				5000 Hr.			
	Rupture		0.5% Creep strain		Rupture		0.5% Creep strain		Rupture		0.5% Creep strain	
	Stress, p.s.i.	Min. creep rate, % per hr.	Stress, p.s.i.	Min. creep rate, % per hr.	Stress, p.s.i.	Min. creep rate, % per hr.	Stress, p.s.i.	Min. creep rate, % per hr.	Stress, p.s.i.	Min. creep rate, % per hr.	Stress, p.s.i.	Min. creep rate, % per hr.
73J(3)	35,000	0.035	Not available		28,000	0.0083	Not available		24,000	0.0031	Not available	
95M255	40,000	0.033	29,500	0.0017	27,000	0.0022	21,000	0.0012	21,000	0.0011	16,500	0.0007
90M158	36,000	0.0025	32,000	0.0022	26,000	0.0016	21,000	0.0014	20,000	0.0008	16,000	0.0006

TABLE XIII

CREEP-RUPTURE DATA AT 815° C. (1500° F.), SUMMARIZED ON A MINIMUM CREEP RATE BASIS

Minimum creep rate, % per hr.	Alloy 73J(3)		Alloy 95M255		Alloy 90M158	
	Stress, p.s.i.	Hours to rupture	Stress, p.s.i.	Hours to rupture	Stress, p.s.i.	Hours to rupture
0.05	37,000	56	42,000	70		
0.01	29,500	570	35,000	300		
0.005	26,000	2,000	32,000	400		
0.002	22,000	10,000	26,000	1,200	32,000	200
0.001	20,000		20,000	5,000	22,000	3,000

Metallography of Creep-Rupture Test Bars

The microstructures of the test bars produced from the alloys listed in Table IX are presented in Figs. 26 to 39.

To reveal the complete microstructure of Alloy 53M104, as shown in Figs. 26 and 27, a double etching technique was employed. An alcohol solution of ferric chloride and hydrochloric acid was used to bring out the light gray areas but this reagent alone would not clearly reveal the eutectic network. In order to bring out this eutectic network an electrolytic etch was employed, using an aqueous solution of sodium cyanide as the electrolyte. With this etch it was necessary to use care to avoid over-etching. About 5 to 15 secs. at 1 to 3 v. was adequate. Neither the electrolytic etch nor the acid etch alone revealed the complete microstructure.

Alloys 90M158 and 95M255 etched satisfactorily with the electrolytic technique alone (see Figs. 28 to 31 and 34 to 37). However, as a further aid in studying the phases present in these alloys and also in studying structural changes that took place during creep-rupture testing, Figs. 32 and 33 are included. These show the microstructure of Alloy 90M158 at 1500 diameters as revealed by a modified chrome-regia etch.

It was found difficult to reveal the microstructure of Alloy 258M252 in a satisfactory manner. The reagent selected, nitric acid plus acetic acid in acetone, seemed to be the most effective.

Discussion of Metallography as Related to Creep-Rupture Properties

At this stage it is not possible positively to identify all phases revealed in the microstructure of the alloys studied.

The electrolytic etch has shown that a phase that occurs in a eutectic manner is common to Alloys 53M104, 90M158, and 95M255. This phase is attacked and darkened by this electrolytic etching. Figs. 26 to 31 and 34 to 37 will illustrate this point. The identity of this phase has previously been tentatively established as NiMo.

It will be noted that the matrix of Alloy 53M104 (see Figs. 26 and 27) consists of a gray etching phase and a clear white phase. This gray phase is etched by the ferric chloride – hydrochloric acid etch and has been tentatively identified as NiAl. It is significant that this alloy, 53M104, which is the only alloy tested that contains this NiAl phase, yielded the poorest creep-rupture properties. A similar etching technique applied to Alloys 90M158, 95M255, and 258M252 failed to reveal a similar phase.

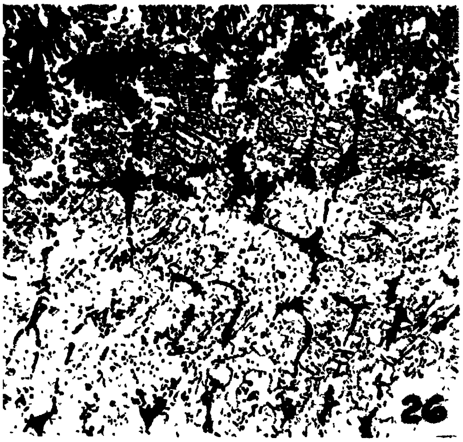
The two alloys that gave the best creep-rupture performance at 1500° F. possessed similar microstructures, as may be seen from Figs. 28 to 31 and 34 to 37. This microstructure consists of:

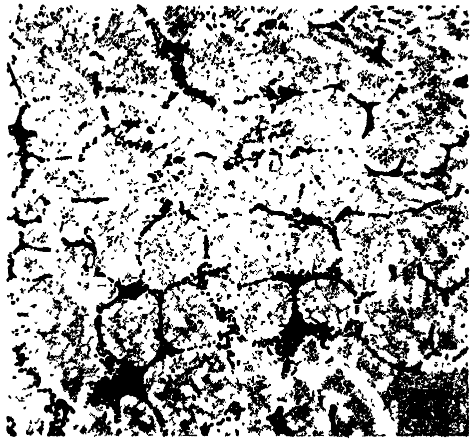
(*a*) The previously mentioned NiMo eutectic phase that is darkened by the electrolytic etch.

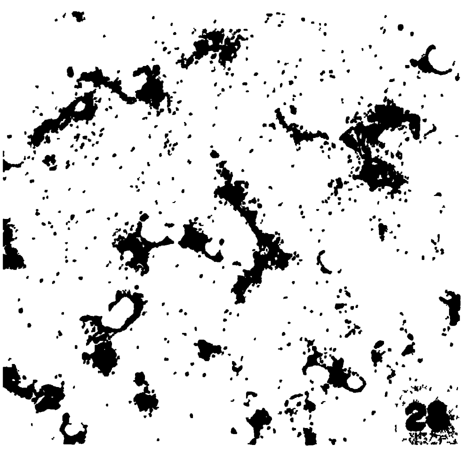
(*b*) Clear white areas usually associated with NiMo eutectic. By reference to Fig. 10, these areas are tentatively identified as Ni_3Al and were originally the alpha-Ni_3Al eutectic (1).

(*c*) A mottled background that at a high magnification (see Figs. 29, 32, and 35) is seen to be a dark-etching, very fine network in a white background. The network is tentatively identified as Ni_3Al and the background as alpha (see Figs 10 and 11).

The clear white areas of Ni_3Al are more numerous in Alloy 90M158 and the NiMo eutectic is more prevalent and continuous in Alloy 95M255 (see Figs. 28 and 34). It is considered significant that these two microstructural features are always associated with each other; this helps to confirm the possibility that the clear Ni_3Al areas are eutectic in origin.







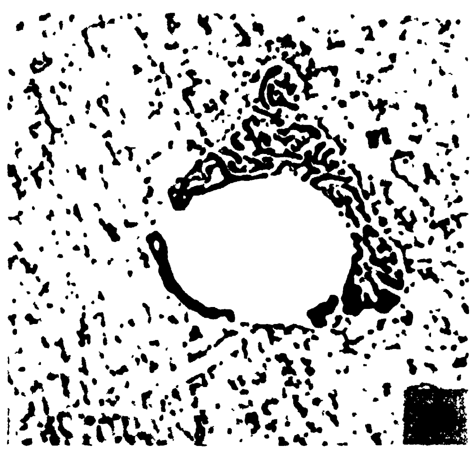


FIG. 26. *Alloy 53M104, as cast. Etched five seconds in ferric chloride plus hydrochloric acid in alcohol, and 15 sec. electrolytically in 10% sodium cyanide at 3 v. ×200. Ni, 74.9%; Al, 14.2%; Mo, 10.4%.*

FIG. 27. *Alloy 53M104, after creep-rupture test at 1500° F. for 27 hr. Etched five seconds in ferric chloride plus hydrochloric acid in alcohol, and 15 sec. electrolytically in 10% sodium cyanide at 3 v. ×200. Ni, 74.9%; Al, 14.2%; Mo, 10.4%.*

FIG. 28. *Alloy 90M158, as cast. Electrolytic etch: 10% sodium cyanide at 3 v. ×200. Ni, 75.6%; Al, 8.4%; Mo, 15.8%.*

FIG. 29. *Same as Fig. 28. ×1500.*

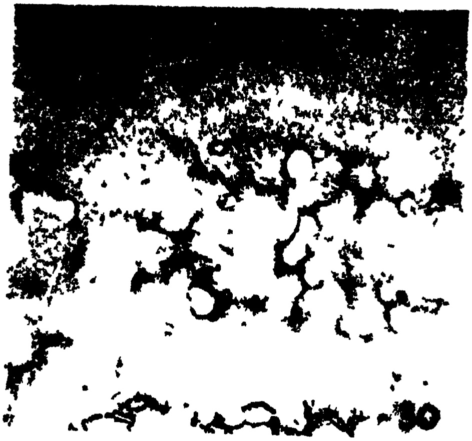
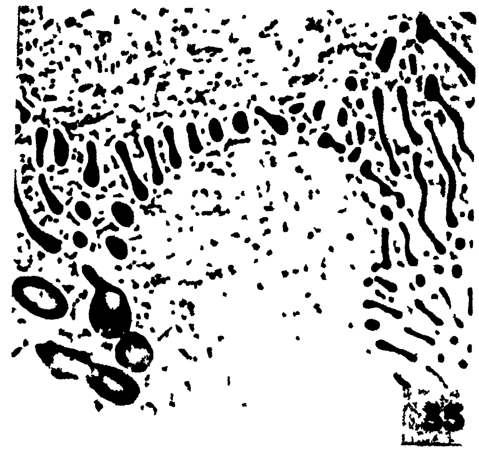


FIG. 30 *Alloy 90M158, after creep rupture testing at 815° C (1500° F) for 680 hr Electrolytic etch in 10% sodium cyanide at 3 v* ×200

FIG. 31 *Same as Fig 30* ×1500.

FIG. 32 *Alloy 90M158, as cast Etchant alcoholic chrome regia* ×1500

FIG. 33 *Alloy 90M158, after 680 hr creep rupture testing at 815° C (1500° F). Etchant alcoholic chrome regia.* ×1500.



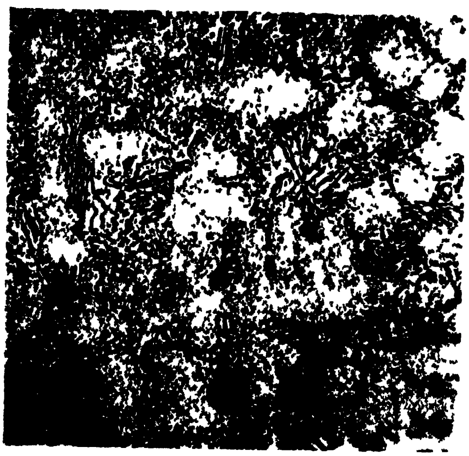


FIG. 34. *Alloy 95M255, as cast. Electrolytic etch: 10% sodium cyanide at 3 v. ×200. Ni, 66.5%; W, 7.0%; Mo, 25.5%.*

FIG. 35. *Same as Fig. 34. ×1500.*

FIG. 36. *Alloy 95M255, after creep-rupture testing at 815° C. (1500° F.) for 930 hr. Electrolytic etch: 10% sodium cyanide at 3 v. ×200.*

FIG. 37. *Same as Fig. 36. ×1500.*

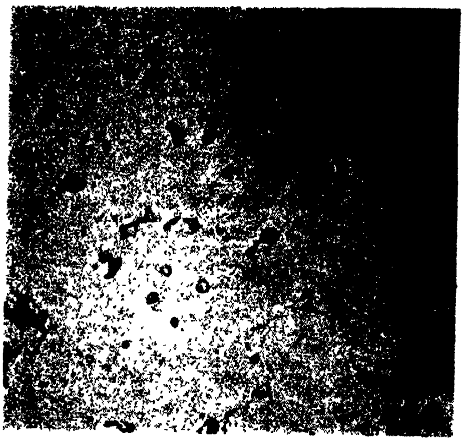


FIG. 38. *Alloy 258M252, as cast. Etch: nitric acid plus acetic acid in acetone. ×200. Ni, 72.4%; Al, 2.8%; Mo, 25 2%.*

FIG. 39. *Alloy 258M252, after creep-rupture testing at 815° C. (1500° F.) for 460 hr. Etch: nitric acid plus acetic acid in acetone. ×200. Ni, 72.4%; Al, 2.8%; Mo, 25.2%.*

After exposure to the temperature of testing at 815° C. (1500° F.) there is evidence that the Ni_3Al network has coalesced. A comparison of Fig. 29 with Fig. 31, and of Fig. 35 with Fig. 37, will illustrate this.

Further to study the phases present in Alloys 90M158 and 95M255, various other etching reagents were employed. A modified alcoholic solution of chrome-regia seemed to be the most useful. The microstructures of Alloy 90M158 (as developed by this reagent), both before and after creep-rupture testing, are shown at a magnification of ×1500 in Figs. 32 and 33. The NiMo eutectic phase that was darkened by the electrolytic etch was only outlined by the chrome-regia etch. The network structure shown in Fig. 29 has been brought out more clearly by this chrome-regia etch in Fig. 32. The effect on this network of prolonged exposure to a temperature of 815° C. (1500° F.) is well illustrated by Fig. 31. Here the coalescence of this network phase is unmistakable.

The fourth alloy tested, 248M252, is not of much interest since its properties were quite inferior. Its microstructure, as shown in Fig. 38, is largely single-phase, probably alpha solid solution, with small patches of a second phase which can be resolved into a eutectic-like appearance at high magnification. The microstructure is radically altered during creep-rupture testing, as may be seen in Fig. 39. From a study of Ellinger's work (2), this new phase in Fig. 39 would appear to be the nickel–molybdenum phase, gamma (Ni_3Mo).

General Conclusions

It is evident that the work reported in this paper has provided the starting point for the development of an entirely new series of high temperature alloys based on nickel, aluminum, and one or more other elements, such as molybdenum.

There is evidence that the microstructure of these alloys may be used as a criterion of their usefulness, since any alloy containing an appreciable proportion of the phase NiAl would not be expected to be suitable.

While most of the data presented are only the results of single melts and single tests, the indications are nevertheless quite promising. One of the alloys produced (95M255) compares quite favorably with the best of other known high temperature alloys. Alloys of this new series are readily melted by high frequency induction and present no unusual casting difficulties.

Acknowledgments

This work has been made possible through the co-operation of the Bureau of Mines and the National Research Council's Associate Committee on High Temperature Metals. Grateful acknowledgment is made for assistance and advice received, during the preparation of this paper, from H. H. Bleakney,

Associate Research Officer of the National Research Council and secretary of the Associate Committee on High Temperature Metals. It is also desired to acknowledge the work of R. F. Cole, presently of the Ford Motor Company of Canada, Limited, who assisted in the earlier stages of this project.

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MEASURING THE SOLIDS CONTENT OF HONEY AND OF STRAWBERRY JAM WITH A HAND REFRACTOMETER[1]

BY JESSE A. PEARCE[2] AND SUZANNE JEGARD[2]

Abstract

A hand refractometer may be useful for routine inspection of the solids content of honey, and of strawberry jam containing added pectin. For 76 pairs of determinations on honey,

$$y = 1.116x - 7.58,$$

with a standard error of prediction of $\pm 0.4\%$; for 116 pairs of determinations on the jam,

$$y = 1.022x - 0.79,$$

with a standard error of prediction of $\pm 0.3\%$, where y is the per cent solids by the A.O.A.C. vacuum-oven method and x is the reading on the hand refractometer. A standard error of $\pm 0.5\%$ was observed for determinations by the vacuum-oven method, and of $\pm 0.4\%$ for determinations with the hand refractometer.

Introduction

The solids content of products such as honey and jam can be readily determined by the vacuum-oven method (1, p. 582) or with an Abbé refractometer (2). While neither method is suitable for field inspection, determinations using a hydrometer (3) have been reasonably satisfactory for inspection work. Since relatively inexpensive hand refractometers have provided a simple and rapid method of determining egg solids under field conditions (4), these laboratories were asked to calibrate a hand refractometer in terms of the solids content of honey, and of strawberry jam containing added pectin. This paper describes these calibrations.

The Hand Refractometer

The hand refractometer used in this work was manufactured by the Bausch and Lomb Optical Company, Rochester, New York. It is calibrated for sucrose solutions containing from 40 to 85% solids, and the scale can be read within $\pm 0.2\%$ at solids contents of about 40% and within $\pm 0.1\%$ at 80%. The refractometer is designed for use at 68° F. (20° C.) and has a correction thermometer attached, which is calibrated in per cent sucrose according to the temperature coefficient for the refractive index of sucrose solutions.

[1] *Manuscript received October 27, 1948.*

Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as Paper No. 222 of the Canadian Committee on Food Preservation and as N.R.C. No. 1885.

[2] *Biochemist, Food Investigations.*

Application to Honey

Since the temperature coefficient for the refractive index of sucrose solutions differs slightly from that for honey (0.00018 and 0.00023 respectively per degree Centigrade), readings on honeys of different solids content were compared at temperatures of 40°, 60°, 80°, and 100° F. (4°, 16°, 27°, and 38° C.). Table I shows that the correction thermometer on the instrument can be used with reasonable accuracy over this temperature range; but that vague lines, dividing the light and dark fields in the refractometer, interfered with the measurement at 100° F. Temperatures between about 60° and 80° F. gave the best results and all further measurements on honey were made within these limits.

TABLE I

VARIATION IN HAND REFRACTOMETER READINGS, %, WITH TEMPERATURE OF HONEY

Sample	Solids, at various temperatures, °F.			
	40	60	80	100♀
1	♀♀	♀♀	♀♀	86.1
2	♀♀	♀♀	86 4	86.1
3	♀♀	85 0	85 0	84.8
4	♀♀	84.3	84.2	84.1
5	♀♀	83.8	83 8	83.6
6	82 0	82.1	82.1	81.9
7	81 4	81.6	81.3	81.4
8	79.1	79.1	79.0	79.1
9	78.6	79.5	79.3	77.7
10	77.0	77 2	77 1	77 2
11	76.7	76.7	76.4	76.6

♀ *Readings difficult, double line formed in refractometer.*
♀♀ *Line in refractometer too vague to permit a valid reading.*

Vague lines observed for concentrated honeys held at low temperatures were attributed to partial crystallization of the sugars. Comparative measurements on samples of fluid and crystalline honeys containing 75 to 80% solids showed that crystallized honey gave hazy lines in the refractometer and could not be used for this test. All further work was done on fluid honey.

Tables relating solids content of honey by the A.O.A.C. vacuum-oven method and refractive index on an Abbé refractometer have been published (2). These data were converted to readings on the hand refractometer at 68° F. to give the curve shown in Fig. 1. Honey was diluted to give a range of solids from 76 to 88%, determined by the vacuum-oven method, and the mixtures were examined in the hand refractometer. The results are given as points on Fig. 1; they show close agreement between the previous and present techniques, and support the use of the hand refractometer.

To assess the application of this instrument, the solids in 76 samples of honey obtained in routine inspections were determined by the vacuum-oven method and with the hand refractometer. The samples were obtained during

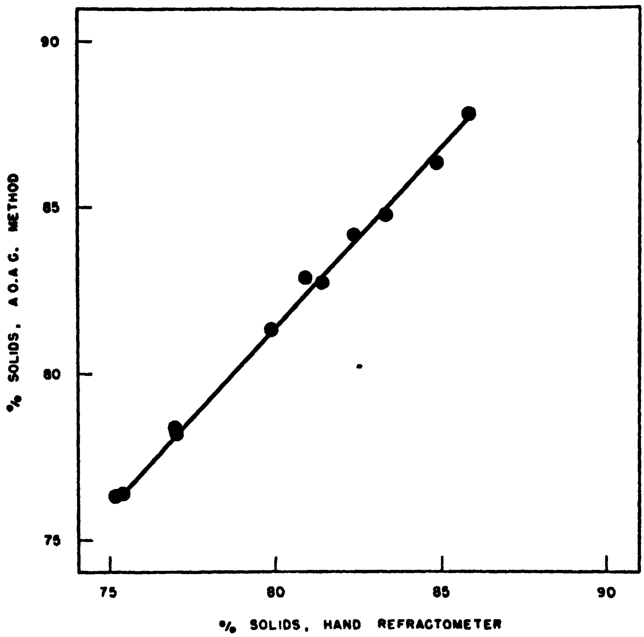

FIG. 1. *Relation between solids in honey as determined by the A.O.A.C. vacuum-oven method and by the hand refractometer.*

Solid line—values converted from refractive indices in Ref. (2).

Points—values determined in course of present study.

1946 and 1947 from all Canadian provinces but New Brunswick and Prince Edward Island and were classed as white, golden, light amber, dark amber, and dark. Statistical analysis showed that, in general, the color of the honey and the year of production had little effect on the measurement, but that honey of the same color from different provinces gave equations that were significantly different. For example, the regression lines for golden honey from different provinces, shown in Fig. 2, are statistically different, but the maximum difference between the curves is about the same order as the standard error ($\pm 0.4\%$) of an equation for 76 samples,

$$y = 1.116x - 7.58$$

where y is the per cent solids by the vacuum-oven method and x is the hand refractometer reading.

Application to Strawberry Jam Containing Added Pectin

The solids in fluid honey can be determined without preliminary separation, but the solids in jams are usually determined on a separated fluid that is as free as possible from suspended matter. In this work, separation was effected

by straining juice from the jam through muslin bolting cloth No. 12XX (1, p. 381). The solids in the strained liquid were determined by the hand refractometer, and by the A.O.A.C. vacuum-oven procedure (1, p. 556), but using sand in the moisture tins (1, p. 557).

Although the solid material in fluid separated from jam is primarily sucrose, the correction thermometer on the hand refractometer was checked by readings on four jams, ranging in solids from 62 to 71%, at temperatures of 40°, 60°,

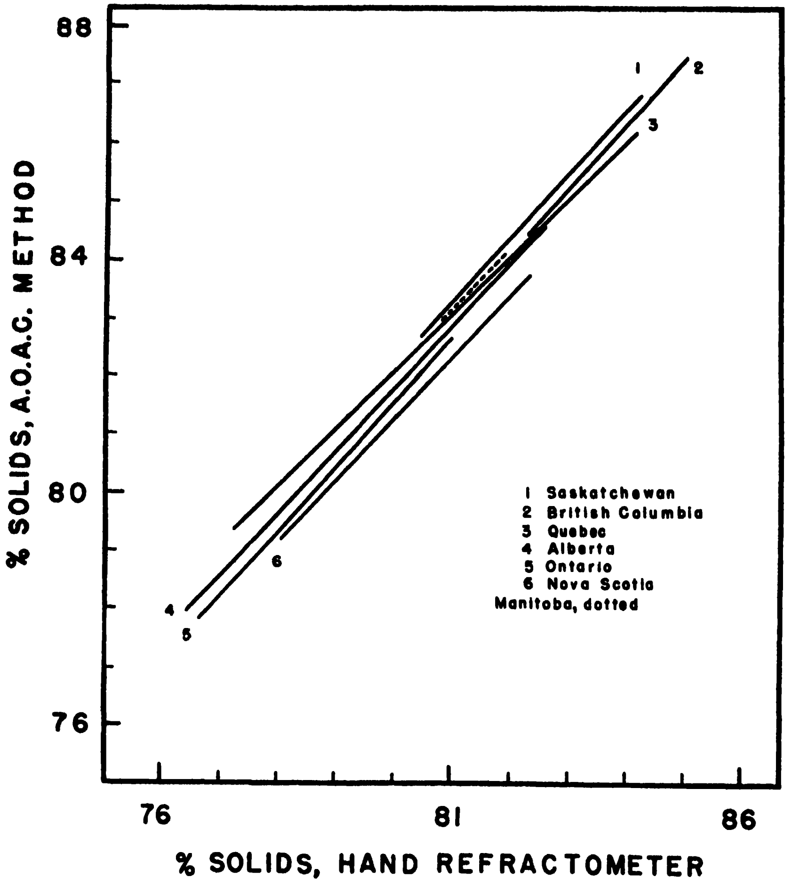

FIG. 2. *Relation between solids in golden honeys, by provinces, as determined by A.O.A.C. vacuum-oven method and by the hand refractometer.*

80°, and 100° F. The averages were 66.8, 66.6, 66.3, and 67.0% at the four respective temperatures, with a necessary difference of 0.4%*. Consequently, a temperature range from 60° to 80° F. is recommended when using the hand refractometer for inspection work.

To determine the error in either method and the relation between the two methods of measurement, 29 one-pound samples of strawberry jam with added

* *Five per cent level of statistical significance.*

pectin were collected during routine inspections, and each sample was divided into four parts, which were placed in sealed containers. Single measurements of the solids content were made on different days on each part of each sample by both techniques.

For the 116 pairs of measurements on these jams, which ranged from 61% to 72% in solids, the relation between the per cent solids by vacuum-oven method (y) and the hand refractometer reading (x) was

$$y = 1.022x - 0.79,$$

with a standard error of prediction of $\pm 0.3\%$.

The vacuum-oven method, which is usually considered to be the reference method, had no greater accuracy than the hand refractometer. An examination of the data for jams showed that solids contents were determinable by the vacuum-oven method with a standard error of $\pm 0.5\%$, and by the hand refractometer with a standard error of $\pm 0.4\%$.

Acknowledgments

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THE FLUIDIZATION TECHNIQUE APPLIED TO DIRECT DISTILLATION OF OIL FROM BITUMINOUS SAND[1]

By P. E. Gishler[2]

Abstract

The fluidized solids technique has been applied successfully to the flash distillation of oil from Alberta bituminous sand on a laboratory scale. At 500° C. a 76% oil recovery was obtained. The remaining 24% produced approximately equal weights of coke and gaseous compounds. At temperatures below 460° C. trouble was experienced in maintaining a fluidized bed because of the slow rate of distillation. As temperatures were increased above 500° C. the yield of oil decreased, with a corresponding increase in gas formation.

Introduction

The use of a fluidized solids bed as a process tool is expanding rapidly. Its chief value lies in its applicability to reactions where a uniform temperature and good heat transfer are required. In reactions requiring a catalyst, a tremendous surface area under controlled conditions is made available.

The first extensive application has been in the catalytic cracking of oil (7). Here, the catalyst, in a finely divided state, forms the fluidized solids bed. The oil vapor to be cracked serves as the fluidizing agent. Another application has been in the calcining of limestone where the combustion gases fluidize the bed of lime (1), oil being fired directly into the fluidized bed. Recently, work has been published on its use in the distillation of oil from oil shale (8). Shale is a rocklike material that can be crushed and sized and in this respect it differs from Alberta bituminous sand, which consists of sand particles coated by a film of viscous bituminous oil. This exists in more or less firmly compacted beds of tremendous extent and considerable depth in an area bordering the Athabaska River in northern Alberta (5). Recently, an unusually rich deposit has been outlined in the Mildred Ruth Lake area (6).

There have been a number of attempts at developing equipment that would recover the oil content of these sands by distillation methods (5). These have failed, owing mainly to the difficulties resulting from the sticky nature of the bituminous sand and its extremely low heat transfer coefficient. In a more successful approach to the recovery of oil from bituminous sand, hot water has been used as the separating medium. This method of separation, with different modifications, has been studied extensively, both on a laboratory and semicommercial scale. Comprehensive reviews have been published (2, 3, 4, 5).

Fluidization

The fluidization technique has made it possible to carry out certain operations that would meet with difficulties in other conventional forms of apparatus.

[1] *Manuscript received November 15, 1948.*

Contribution from the Applied Chemistry Branch, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1886.

[2] *Chemist.*

A number of preliminary tests were therefore carried out in order to determine whether this technique could be successfully applied to the direct distillation of oil from Alberta bituminous sand.

The first experimental fluidizing unit was simply a 2 in. glass tube, 2 ft. long, drawn to a cone at the bottom end and open at the top. This was wound with resistance wire and insulated, except for a narrow area at the front and back, which served as a window. A 6 in. depth of sand constituted the fluidizing bed. A stream of preheated nitrogen was passed upwards through the bed in an amount sufficient to keep the bed in vigorous agitation. Tests were carried out in the temperature range 400° to 500° C.

The object was to gain information on the rapidity with which the oil could be distilled from the bituminous sand and to study the behavior of lumps of bituminous sand of varying size and compactness when they were dropped into the hot fluidized bed. The following information was gained:

(i) At 500° C. distillation was rapid. Heavy oil fumes were swept by the nitrogen stream out of the unit as soon as a lump was dropped into the bed, and fuming was completed in several seconds. The lumps, ranging in diameter from $\frac{1}{8}$ in. to 1 in., appeared to disintegrate to individual sand grains immediately on entering the bed. Each grain was coated with a thin closely adhering film of coke.

(ii) At 400° C. distillation was slower and the lumps fed to the still did not disintegrate as readily as at the higher temperature. Trouble was experienced with agglomeration.

The results of these preliminary tests indicated that the problems of heat transfer and handling encountered in other types of direct distillation apparatus could be overcome in a fluidized bed. Apparatus was therefore built to permit a quantitative study of direct distillation by this method. This might be considered as one step in a two step method of oil production consisting of:

(i) Flash distillation of oil in a fluidized bed,

(ii) Burning of the coke from the residual sand to generate the necessary heat for the distillation step.

Experimental

The work reported here consisted of a series of direct distillations of bituminous sand carried out at different temperatures. The yields of oil, coke, and gas were determined. The following analyses were carried out on the oil: distillation, density, viscosity, and total sulphur.

The apparatus is shown in Fig. 1. It consisted of a cylinder of nitrogen, which served as the fluidizing gas, a nitrogen preheater, a still containing a fluidized sand bed, a trap, an electrical precipitator, and an activated charcoal tower with auxiliary steaming equipment.

The still consisted of a stainless steel tube 3 ft. long and 2.5 in. in diameter, with a perforated plate 2.5 in. from the bottom to hold the charge and distribute the preheated nitrogen. A 1 in. tube welded to the plate served to draw

off the spent sand. Four thermocouples were placed as indicated. Three separate resistance coils surrounding the still supplied the required heat. The water cooled trap cooled the offgases and prevented any surge of dust from

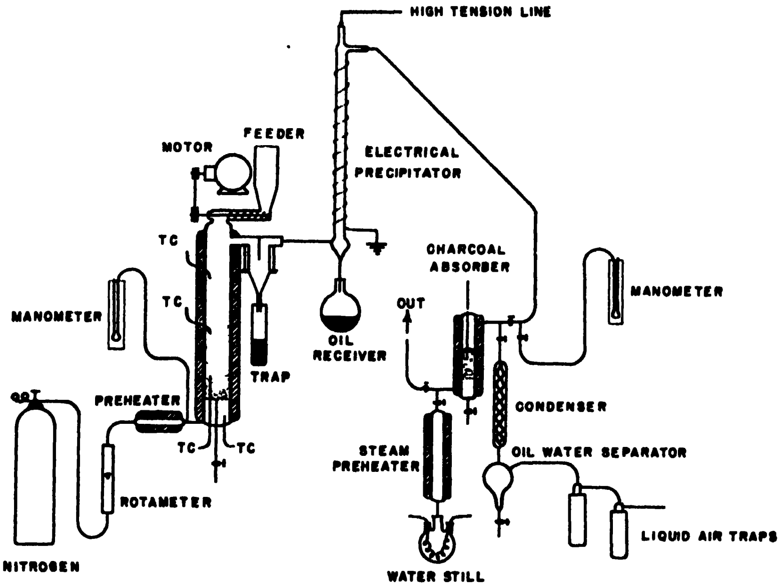

FIG. 1. *Apparatus for direct distillation of bituminous sand in a fluidized sand bed.*

reaching the remainder of the collection system. About one-third of the heavy oil and a small amount of carbon and fine dust were removed by the trap. The remainder of the heavy oil, which was in the form of a suspension in the offgas, was effectively removed by the electrical precipitator. The activated charcoal scrubber removed the light oil (mainly gasoline) and a part of the hydrocarbon gas fraction. This was recovered by steam distillation.

At the start of a run sufficient spent sand from a previous run was poured into the still to form a bed depth of 6 in. Nitrogen preheated to the distillation temperature was introduced at a rate sufficient to fluidize the bed. Gas rates were measured by means of a rotameter. The heaters were turned on and when the desired temperature was reached bituminous sand was fed continuously into the bed from a worm feeder. A charge of about 3000 gm. was used for each run. The spent sand bed was allowed to build up to 10 in. and maintained there by periodic removal through the 1 in. tube. This flowed freely from the system when the gate valve on the tube was opened. The behavior and depth of the bed could be determined by observing the manometer indicated in Fig. 1. Feed rates were 2000 to 2500 gm. per hr., the lower rates being necessary at the lower temperatures.

At the completion of a run the heavy oil was collected and measured. The light oil was steam distilled from the charcoal. The volatile fraction was caught in two liquid air traps placed in series.

Results

The bituminous sand used for these tests had a bitumen content of 16%, which is higher than the average for the field. This was supplied by the Bureau of Mines and consisted of drill cores obtained from the Mildred Ruth Lake district near the Athabaska River in Alberta. This material, although mined about one year ago, had a fresh, unweathered appearance.

Tests have also been made on freshly mined coarse bituminous sand from the Bitumount area and on fine, badly weathered sand from near Waterways. The results indicate that percentage recovery of oil does not vary appreciably with variation in the physical condition or oil content of the sand.

The results showing the influence of temperature on yields and physical properties are shown in Table I and Fig. 2. Yields are expressed as cubic centimeters of oil recovered per 100 cc. bitumen content in the bituminous sand feed.

TABLE I

INFLUENCE OF TEMPERATURE ON OIL RECOVERY

Run No.	16	15	13	10	17	11	14	12	18
Temperature, °C.	425	450	460	475	500	525	565	600	700
Bitumen in feed, cc.	100	100	100	100	100	100	100	100	100
Recovery heavy oil, cc	62	68	74	71	73	63	52	33	21
Recovery light oil, cc	2	2	2	3	3	6	9	10	10
Oil yield, vol %	64	70	76	74	76	69	61	43	31
Coke in sand, wt %	—	2.0*	2.0	2.0	1.9	1.8	1.8	1.7	3.3
Heavy oil analysis									
Specific gravity, 60° F /60° F.	.965	.975	.967	.971	.975	.978	.992	1.058	1.158
Viscosity, centistokes,									
100° F.	133	249	101	137	135	66	43	41	—
32° F.	6018	11300	2779	4254	4253	1381	699	902	—
Sulphur, %	4.03	4.41	3.91	3.88	3.86	4.08	4.29	5.00	3.13

* *Coke determined on free flowing sand only, lumps screened out.*

Highest yields were obtained in the temperature range 460° to 500° C. At lower temperatures, distillation was incomplete and a properly fluidized bed was difficult to maintain owing to lumping up of the charge. Above 500° C., cracking became progressively more severe, resulting in increased formation of light oil and gas. A temperature of 500° C. may be considered as the

optimum when both ease of operation and yield are considered. Expressed in terms of bituminous sand of 16% bitumen content, 1 ton of bituminous sand will produce 0.7 bbl. of oil, free of water and solids.

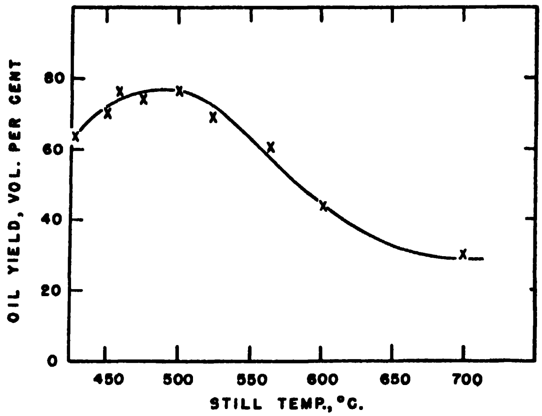

FIG. 2. *Oil recovered from bituminous sand.*

The oil had a high specific gravity, was quite fluid at room temperature, and was high in sulphur. Suspended solids amounted to 0.1% by weight. Distillation data are given in Table II.

TABLE II

DISTILLATION OF HEAVY OIL PRODUCED IN FLUID STILL

Run No.	16	15	13	10	17	11	14
Initial boiling point, °F.	382	415	290	380	373	300	259
5% recovered, °F.	513	523	464	499	474	426	405
10% "	549	558	533	553	537	603	464
20% "	587	602	599	594	591	564	529
30% "	623	619	628	614*	613	562*	590
40% "	637	614	640	606	626		613
50% "	647	612*	647	594	622*		613*

* *Evidence of cracking.*

A sample of heavy oil produced in a run at 500° C., using bituminous sand from Bitumount, 55 miles north of Waterways, was distilled at 10 mm. pressure. The data corrected to atmospheric pressure are given in Table III.

TABLE III

DISTILLATION OF HEAVY OIL AT LOW PRESSURE (CORRECTED TO 760 MM.)

5% - 442° F.	40% - 676° F.
10% - 498	50% - 745
20% - 568	55% - 752
30% - 617	

Two light oil samples were accumulated. Sample 1 included runs at 500° C. and lower. Sample 2 included runs at 565° C., 600° C., and 700° C. Distillation data are shown in Table IV.

TABLE IV

DISTILLATION OF LIGHT OIL

Distillation	Sample 1	Sample 2
Initial boiling point, °F.	97	86
5% recovered, °F.	104	91
10% "	117	131
20% "	151	163
30% "	181	183
40% "	201	201
50% "	217	217
60% "	235	234
70% "	255	250
80% "	279	273
90% "	324	338

Gas Formation

Aside from the gasoline fraction, the activated charcoal also removed the heavier gaseous hydrocarbons formed by cracking. On steam distilling of the charcoal, these were caught in two liquid air cooled traps. The volumes recovered, however, could not be used to determine gas production quantitatively because the efficiency of the charcoal absorber was not known. To determine gas yields the following apparatus was therefore set up (Fig. 3).

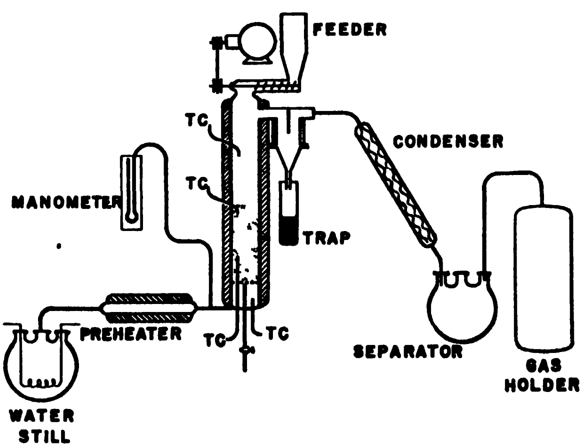

FIG. 3. *Apparatus to determine yield of gaseous products.*

Steam was used as the fluidizing gas. This was produced at known rates in an electrically heated steam generator. The steam preheater, still, and trap were the same as used for the experiments described above. The trap and a large water cooled condenser removed the steam and the bulk of the oil. The light hydrocarbons and hydrogen passed through to a gasometer, where their volume was measured. Bituminous sand was fed at a known rate into the still so that gas production could be determined quantitatively. The temperature range 465° to 600° C. was studied. The results are shown in Fig. 4.

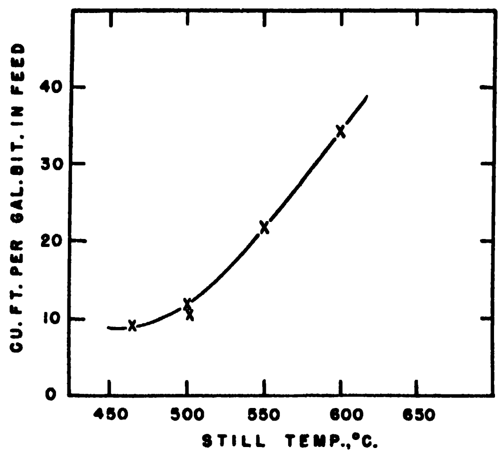

FIG. 4. *Gas formation due to cracking.*

Accurate and complete analyses of the gases were impossible under the conditions of the experiments, owing to high sulphide gas content. On a Burrell gas analysis apparatus, results varied considerably. These indicated, however, that the amounts of saturated and unsaturated hydrocarbons were about equal, amounting to approximately 40% each on a sulphide free basis. The hydrogen content was approximately 15%.

The above described method of producing a petroleum distillate by direct flashing of oil from tar sands is believed to be a simplified approach to the problem of utilization of the bituminous sand deposits. The data presented, however, cannot be used to determine capacities or costs. These must await pilot scale operation data. A search of the literature would indicate that further data are also required on the various other methods of extraction that are under study, before a comparative analysis can be made.

Acknowledgment

Thanks are due to Mr. A. Lafortune and Mr. Neil Scheel for their assistance in carrying out these experiments.

The author also wishes to acknowledge with thanks the co-operation of the Bureau of Mines and of Dr. K. A. Clark of the Research Council of Alberta for supplying bituminous sand samples.

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THE WEATHERING CHARACTERISTICS AND ROT RESISTANCE OF COTTON DUCK TREATED WITH THE COPPER COMPLEX OF NITROSOPHENYLHYDROXYLAMINE[1]

By C. H. Bayley[2] and Muriel W. Weatherburn[2]

Abstract

Unbleached cotton tentage duck treated with the copper and copper-iron complexes of nitrosophenylhydroxylamine showed considerable resistance to rotting in soil burial tests but gave evidence of enhanced actinic degradation and loss of treating compound as a result of outdoor weathering for three months during the summer. With samples containing a higher concentration of the complexes this degradation was more severe.

The efficacy of a number of organic compounds, capable of forming chelate copper complexes, in protecting cotton tentage duck from microbiological attack, has recently been examined by Illman and coworkers (5). In this work, in which resistance to microbiological attack was measured by noting the ability of the treated fabric to withstand deterioration during soil burial, it was found that the copper complex formed with ammonium nitrosophenylhydroxylamine ("Cupferron") conferred a high level of resistance. It has been shown previously (2) that the weathering characteristics of rot resistant treatments are of importance where the treated fabric is expected to withstand the effects of outdoor exposure. In this connection, the extent to which the treatment is removed by weathering, or tends to influence the actinic deterioration of the fabric, is of considerable importance in assessing the merit of a given treatment. It was therefore of interest to examine in some detail the weathering characteristics of the copper complex of nitrosophenylhydroxylamine when applied to cotton duck. This has been done for (*a*) two concentrations of the complex (Samples *A* and *D*), (*b*) a mixture of the complex and a standard cuprammonium treatment (Sample *B*), and (*c*) a mixture of the copper and iron complexes (Sample *C*). For purposes of comparison, the weathering characteristics of a sample of the duck carrying a standard cuprammonium treatment were also investigated (Sample *E*). The maximum copper content of the samples investigated was around 0.5% (Samples *A*, *B*, and *E*), since this content of copper is similar to that used in commercial treatments.

The samples were tested for rotproofness by the soil burial method before and after weathering by measuring the loss in breaking strength resulting from two and four weeks' burial. In addition, measurement was made of the loss of copper and of the increase in cuprammonium fluidity occurring during weathering.

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1891.

[2] *Chemist.*

Materials Used

The fabric was an unbleached cotton tentage duck weighing 10 oz. per square yard, similar to that used in previous work (2). The Cupferron was obtained from Eastman Kodak Company. The copper acetate ($Cu(C_2 . H_3O_2)_2H_2O$), copper sulphate ($CuSO_4 . 5H_2O$), and ferric ammonium sulphate ($Fe_2(SO_4)_3\ (NH_4)_2 . 24H_2O$) were of technical grade.

The fabric was wetted out in a 0.1% solution of technical sodium lauryl sulphate (Gardinol WA was used) and well rinsed in water. The treatment was then applied at room temperature by a two-bath process in which the fabric in the form of a loop was passed through an aqueous solution of Cupferron for 15 min. using the motor driven rubber covered rolls of a laundry wringer, and then through the solution of the metallic salt or mixture of salts for 15 min. The impregnated fabric was rinsed for two hours in running tap water and air dried. The copper contents of the treated fabric were determined as previously (3). It might be noted that the amount of copper fixed on the fabric by use of copper and iron salts plus Cupferron was considerably lower than that fixed by the same concentration of copper and iron salts plus soda ash, as used in another experiment (6).

Test Methods

The procedures for carrying out the leaching and burial treatments and for determining breaking strengths and cuprammonium fluidity were as previously used (1). The results of a statistical analysis of the breaking strength data indicated that for statistical significance at the 5% level with 10 breaks carried out on each sample, the necessary differences were as follows: leached samples, 17 lb.; weathered samples, 10 lb.; samples leached and buried four weeks, 21 lb.; samples weathered and buried two and four weeks, 16 lb. It was found that breaks occurring at the jaws of the machine gave lower and somewhat more erratic values than those occurring at some distance from the jaws; therefore "jaw breaks" were discarded and in those cases in which the full set of 10 breaks was not obtained, owing to jaw breaks, a formula described elsewhere (4) was used to determine the significant difference between the various sets of specimens.

The samples were exposed to outdoor weathering conditions on the roof of the National Research Laboratories, Ottawa, from 12th June to 12th September 1946.

Data

Table I gives the details of the treating solutions used and the copper contents and colors of the treated fabrics. Data for the weather conditions during the weathering period are given in Table II. The data for breaking strengths on weathering and on burial are given in Table III, and the increase in cuprammonium fluidity and decrease in copper content on weathering in Tables IV and V respectively.

TABLE I

CONCENTRATIONS OF TREATING SOLUTIONS AND CHARACTERISTICS OF TREATED FABRIC

Sample	Treatment		% copper on treated fabric	Color of treated fabric	
	Bath No 1	Bath No 2		Munsell notation*	I S.C.C.-N.B.S. Name**
A	Cupferron 25 gm / liter	Copper acetate 20 gm /liter	0 44	6Y,7 7/1 6	Yellowish gray
B	Cupferron 25 gm / liter	Copper sulphate 100 gm /liter treated with ammonium hydroxide (28% NH_3) until blue precipitate just dissolved	0 52	10Y,7 7/2 5	Pale yellow green
C	Cupferron 25 gm / liter	Copper sulphate 87 gm /liter, ferric ammonium sulphate 93 gm /liter	0 13	1Y,7 6/3 5	Weak yellowish orange
D	Cupferron 5 gm / liter	Copper acetate 20 gm /liter	0 26	6Y,8/2	Weak yellow
E	Cuprammonium solution (as in Bath 2 of Treatment *B*)		0 57	8GY 8 2/1 0	Light greenish grey

* *Munsell Book of Color, Munsell Color Co. Inc., Baltimore, Md. (1942).*
** *Judd D. B. and Kelly K. L J. Research, Natl. Bureau of Standards, 23, 355–385 (1939).*

TABLE II

WEATHER CONDITIONS DURING EXPOSURE OF SAMPLES

Period	Mean daily temp., °F.		Rainfall, in.	Bright sunshine, total hours
	Maximum	Minimum		
June 12 – June 15	68	47	0.02	48.6
16 22	74	51	3 49	62.3
23 29	91	62	0	83.7
30 – July 6	81	62	0.37	87.9
July 7 13	80	58	0.88	75.5
14 20	86	55	0.04	71.2
21 27	82	59	1.57	46.3
28 – Aug. 3	86	57	0.44	51.8
Aug. 4 10	91	59	2.25	67.1
11 17	79	62	0.11	46.4
18 24	77	52	1.10	26.5
25 31	77	48	0.44	38.4
Sept. 1 – Sept. 7	74	48	0.10	57.9
8 12	72	50	0.49	26.3
Average	80	55		
Total			11.30	789.9

TABLE III

EFFECT OF WEATHERING AND BURIAL ON BREAKING STRENGTH

Treatment	Breaking strength, lb.							Breaking strength loss, %					
	Orig. leached	*W* 3 mo.	Buried for 2 weeks after		Buried for 4 weeks after		Leached 24 hr. buried 8 wk.	*W* 3 mo.	Buried for 2 wk. after		Buried for 4 wk. after		*L* 24 hr. and buried 8 wk.
			L 24 hr.	*W* 3 mo.	*L* 24 hr.	*W* 3 mo.			*L* 24 hr.	*W* 3 mo.	*L* 24 hr.	*W* 3 mo.	
A. Cupferron (25 gm./liter soln.) + copper	164(9)	98(10)	166(4)*	90(10)	142(8)	0	44(3)*	40	+1	45	13	100	73
B. Cupferron (25 gm./liter soln.) + cuprammonium	162(10)	98(9)	163(3)*	94(10)	84(10)	10(9)	32(4)*	40	+1	42	48	94	80
C. Cupferron (25 gm./liter soln.) + copper + iron	161(8)	96(6)	155(4)*	15(10)	152(9)	0	120(4)*	40	4	91	6	100	25
D. Cupferron (5 gm./liter soln.) + copper	163(9)	107(9)	172(5)*	55(8)	135(9)	0	20(3)*	34	+6	66	17	100	88
E. Cuprammonium	161(9)	90(10)	174(3)*	81(9)	127(9)	42(10)	18(5)*	44	+8	50	21	74	88
Untreated	159(7)	116(6)	0	25(9)	0	0		27	100	84	100	100	100
Necessary difference in av. of 10 breaks for significance at 5% level	17	10	—	16	21	16	—						

* *Total possible, five breaks.* *Note:—Figures in parenthesis represent the number of "good" breaks on which the average has been based, jaw breaks being discarded.*

L = *Leached.* *W* = *Weathered.*

TABLE IV

INCREASE IN CUPRAMMONIUM FLUIDITY ON WEATHERING

Treatment	Fluidity (reciprocal poises)		
	Original	Weathered	Increase on weathering
A. Cupferron (25 gm./liter soln.) + copper	2.3	19.7	17.4
B. Cupferron (25 gm./liter soln.) + cuprammonium	3.6	18.5	14.9
C. Cupferron (25 gm./liter soln.) + copper + iron	2.7	26.3	23.6
D. Cupferron (5 gm./liter soln.) + copper	3.1	20.3	17.2
E. Cuprammonium	3.1	19.9	16.8
Untreated	3.4	12.5	9.1

TABLE V

DECREASE IN COPPER CONTENT ON WEATHERING

Treatment	Copper content, %		Copper loss on weathering, % of orig.
	Original	Weathered	
A. Cupferron (25 gm./liter soln.) + copper	0.44	0.06	86.3
B. Cupferron (25 gm./liter soln.) + cuprammonium	0.52	0.08	84.5
C. Cupferron (25 gm./liter soln.) + copper + iron	0.13	0	100
D. Cupferron (5 gm./liter soln.) + copper	0.26	0	100
E. Cuprammonium	0.57	0.08	85.9

Discussion

It will be seen that the application of the various treatments did not affect the breaking strength of the original fabric.

On weathering, the Cupferron–metal treatments applied from 25 gm. per liter solutions of Cupferron (*A*, *B*, and *C*) showed breaking strength losses of approximately 40%, considerably higher than the loss (27%) shown by the untreated sample. All the treated samples showed increases in cuprammonium fluidity which were considerably greater than that of the untreated fabric. These data indicate that the treated samples suffered considerable actinic degradation during exposure and it would seem that the extent of this degradation shown by the Cupferron treated samples was of the same order or greater than that resulting from the straight cuprammonium treatment.

Substantial losses of copper occurred in all cases, there being complete loss of copper from the samples (*C* and *D*) having the lowest copper contents (0.13 and 0.26%).

The resistance of all the treated fabrics to soil burial with preliminary leaching was considerable, that of the Cupferron plus copper–iron being considerable after eight weeks.

Resistance of the weathered samples to soil burial for two weeks was shown by the samples containing the Cupferron–copper treatments (*A*, *B*, and *D*) and by the cuprammonium treated sample (*E*). The resistance of the samples treated with Cupferron–copper–iron and with the lower concentration of Cupferron–copper was considerably reduced by weathering, probably owing to the removal of copper. When compared with the sample treated with cuprammonium alone, it will be noted that the breaking strength losses of the Cupferron–copper treatments applied from a 25 gm. per liter solution of Cupferron (*A* and *B*) are similar but that the Cupferron–copper treatment applied from a 5 gm. per liter Cupferron solution (*D*) produced a somewhat greater loss. The sample treated with Cupferron–copper–iron (*C*) showed a still greater loss.

The increase in cuprammonium fluidity resulting from weathering was highest with the Cupferron–copper–iron treated sample, the increases shown by the other treated samples being of the same order.

The loss of copper on weathering shown by the Cupferron metal treated samples was similar to or greater than that shown by the cuprammonium treated sample (*E*), the greatest losses occurring with the samples (*C* and *D*) which originally contained the smallest amounts of copper.

It may therefore be concluded that the application to cotton duck of the ammonium salt of nitrosophenylhydroxylamine followed by the precipitation of the copper chelate complex or of the mixed copper–iron chelate compound imparts considerable resistance to rotting as judged by the soil burial test, but that these treatments also cause an increase in the amount of actinic degradation occurring in cotton duck on weathering as compared with that shown by untreated duck, this increase in degradation being of the same order as that produced by a cuprammonium treatment. The chelate copper complex does not show any greater resistance to weathering than does the standard cuprammonium treatment.

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LABORATORY STUDY OF GERMAN BUNA S-3 CHEMICAL RUBBER[1]

By J. W. L. Fordham,[2] A. N. O'Neill,[3] and H. Leverne Williams[4]

Abstract

The German general purpose tire rubber, Buna S-3, differed from the chemical rubber produced in Canada. The study of the polymerization recipe used for this polymer centered around the role of the regulator in the system. The German technique resulted in a system in which the dilute solution viscosity of the polymer remained relatively constant during the reaction. It was found that this system could be duplicated in the laboratory using the equivalents of the German materials. Methods of analysis for diproxid in solution and in latex were investigated. It was observed that the diproxid disappeared very rapidly from the system and the regulating index was found to be similar to that of tertiary amyl mercaptan and to lie between that of *n*-dodecyl and *n*-tetradecyl mercaptan when all were used in the Buna S-3 system. The polymers produced compared favorably with the German polymer as to molecular weight homogeneity, response to heat softening, and other data. Substitution of tertiary amyl mercaptan in the Buna S-3 system resulted in a polymer very similar to that produced using diproxid, and the reaction rate was increased nearly fivefold. The polymer prepared with diproxid and other regulators in this system seemed to be more homogeneous than those prepared by the Mutual formula.

Introduction

Copolymers had been prepared by Hofmann (9) but the true worth of copolymers was revealed in the appearance of Buna S, a copolymer of butadiene and styrene (18, 19, 20, 21).

Buna S possessed reasonably acceptable properties but was exceedingly difficult to process. The practice arose, therefore, of heat softening the polymer before the final compounding (11).

During the shortages of oleates and linoleates the industry had had to use paraffinic fatty acids entirely (0.5 part) and it was found that under those conditions the polymer was much tougher. This toughness could be overcome by adding a regulator, the one which they preferred being diproxid (2, 22, 23, 25) (diisopropylxanthogen disulphide, 0.1 part). The polymer which was produced in quantity by such a system from 1943 on was known as Buna S-3. The copolymer was not only easier to process but the vulcanizates had superior physical properties.

The recipe for Buna S-3 was somewhat similar to the Mutual formula used for GR–S, the wartime Canadian chemical rubber (10, 29, 33, 34). A comparison between the two recipes is given in Table I.

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From the Physical Chemistry Research Laboratory, Research and Development Division, Polymer Corporation Limited, Sarnia, Ont.

[2] *Chemist.*
[3] *Formerly Junior Research Chemist. Present address: Department of Chemistry, Ohio State University, Columbus 10, U.S.A.*
[4] *Research Chemist.*

TABLE I

COMPARISON OF BUNA S-3 AND GR-S RECIPES

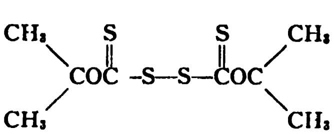
	Buna S-3		GR-S
Butadiene	70 parts		71.5 parts
Styrene	30 "		28.5 "
Water	105 "		180.0 "
Emulsifier			
Nekal BX (SA-178)	4.5 "	S.F. soap flakes	4.3 "
Paraffinic fatty acid	0.5 "		
Sodium hydroxide	0.3 "		
Regulator			
Diproxid	0.1 "	Dodecyl mercaptan	0.45 "
Initiator			
Potassium persulphate	0.45 "		0.23 "
Shortstop*			
Phenyl-β-naphthylamine	3.0	Hydroquinone	0.15 "
Antioxidant*		BLE	1.5*
Coagulant*			
Calcium chloride	6.0	Sodium chloride	12.0
Acetic acid	0.80	Sulphuric acid	0.9
Ferrous sulphate	0.12		

* *Based on 100 parts of copolymer.*

The ratio of styrene to butadiene was greater in the Buna S-3 system because the diproxid was added in portions as a solution in styrene and consequently some of the styrene had to be withheld from the reaction during the initial stages. The water content was considerably less.

The emulsifier consisted of the Nekal BX, paraffinic fatty acid (C_{12}—C_{16}) and sodium hydroxide. The Nekal BX was about 80% pure; the remaining 20% was sodium sulphate—a desirable impurity which aided in preventing precoagulation during polymerization. The paraffinic fatty acid was added to assist in the processing of the rubber during subsequent compounding. Enough caustic was used to neutralize the fatty acid and to bring the pH of the water up to 11–12. The pH would be high enough throughout the entire reaction to ensure a satisfactory rate.

The regulator



was added in three equal portions in a styrene solution at 0, 20, and 40% conversion. It disappeared much faster than did the dodecyl mercaptan (12) in the GR-S system and hence increment addition was a necessity if a uniform raw polymer viscosity was to be maintained throughout the reaction.

The shortstop (stopping agent) used in the Buna S-3 system was phenyl-β-naphthylamine. This compound was not as effective as hydroquinone, and consequently the residual unreacted monomers had to be removed immediately.

However, the phenyl-β-naphthylamine acted as an antioxidant or stabilizer for the rubber also and was the preferred antioxidant when the rubber was to be heat softened.

The coagulants used in the Buna S-3 system were different from those in the GR-S system. Calcium chloride was used in place of sodium chloride because the Nekal-emulsified latex was more stable than the soap-emulsified latex. Acetic acid was used in place of sulphuric acid because the former was volatile and disappeared during drying of the copolymer, leaving no residual acid to attack the cords and fabrics in the final manufactured product. Acetic acid coagulated polymers also heat softened more readily than did sulphuric acid coagulated polymers. The ferrous sulphate was used to catalyze the thermal breakdown. The coagulants and the latex had to be dilute enough to ensure complete coagulation and yet concentrated enough to ensure a large porous crumb suitable for rapid drying.

The reaction was allowed to proceed at about 45° C. until a conversion of 60% was reached, at which time the reaction was stopped by addition of phenyl-β-naphthylamine and the residual monomers were removed. The reaction required 30 to 36 hr. to reach 60% conversion compared with 12 to 16 hr. at 50° C. required for the GR-S system to reach 72% conversion at which time the GR-S reaction is stopped. The Buna S-3 reaction was not allowed to go beyond 60% conversion because of gel formation. Some gel was formed even at this conversion, but it was very loose (swelling volume > 100) and broke down readily on milling or heat softening.

More regulator was not used to give a lower Mooney rubber and make heat softening unnecessary because increasing the diproxid, while decreasing the Mooney, depreciated the physical properties in comparison with those of the underregulated, heat softened copolymer.

Since many polymers became insoluble on coagulation and handling they used latex extraction to obtain solutions for precise measurements on their polymers.

Techniques

The polymerization reaction was carried out in 4- or 8-oz. bottles fitted with metal screw caps and suitable gaskets (14) to permit hypodermic syringe sampling (16), or in 32-oz. crown cap bottles fitted similarly.

The monomers were pre-emulsified with the emulsifier and water by end over end rotation of the bottles for one hour in a bath maintained at 45° to 50° C. The resulting emulsion had a pH of 12. After pre-emulsification the initiator solution was injected into the bottles by means of a hypodermic syringe. Conversion was followed by hypodermic syringe sampling and determination of per cent solids. The regulator was added in varying amounts and at various conversions as a solution of diproxid in styrene. Bottles were removed periodically throughout the reaction, and aqueous solution of hydroquinone (or styrene solution of phenyl-β-naphthylamine) was added as a shortstop and final conversions were determined.

The following procedures were used to characterize the polymer.

For the vistex viscosity (dilute solution viscosity by complete solution of latex in mixed solvents) a 1 ml. sample of latex was taken by means of a 5 ml. syringe. The sample was released into 50 ml. of a rapidly agitated chlorobenzene–pyridine mixture (75 volume % chlorobenzene, 25 volume % pyridine). The solution was transferred to a 100 ml. volumetric flask and made up to the mark. A clear solution was obtained after the mixture had been allowed to stand 15 min. The samples did not need to stand longer than the time for the above manipulations in order to come to equilibrium. This solution was filtered through glass wool. The concentration was determined by evaporating 20 ml. to dryness and weighing the residue. The weight of residue was corrected for nonrubber solids in those experiments so designated. Viscometric flow times were determined at 30° C. on the original solution and on two dilutions with the above solvent mixture. For a blank or "pure solvent" flow time the above procedure was repeated using a sample from a bottle containing an unreacted Buna S-3 emulsion containing all ingredients with the exception of the potassium persulphate.

For the determination of these "three point" viscosities a modification of the Ubbelohde type viscometer was developed. This modification consisted of replacing the small 15 ml. reservoir bulb of the viscometer with a 100 ml. bulb. This permitted all dilutions to be made in the viscometer and eliminated the necessity of rinsing it after each determination.

The following designations were used:

$$\text{Specific vistex } t_{v_{sp}} = \frac{t \text{ solution}}{t \text{ ``blank solvent''}} - 1$$

$$\text{Vistex } [t_v] = \lim_{C \to 0} \frac{t_{v_{sp}}}{C}$$

in which C is in concentration in grams per 100 ml. of solution and t is flow time in seconds. If instead of flow times the kinematic viscosities were used the extrapolation gave the intrinsic vistex viscosity $[\eta_v]$. Later the method was modified by using 80/20 benzene/isopropanol mixture and finally modified again by using the 80/20 benzene/isopropanol mixture but diluting with benzene rather than with the mixture. The latter method gave the true intrinsic viscosity or intrinsic flow time. Direct extraction of the latex with benzene or cyclohexane did not achieve satisfactory results but was sufficiently promising to suggest further development.

To determine the intrinsic flow time and gel content of the dry polymer the remainder of the latex from each bottle, containing 1.5% antioxidant based on the polymer present, was steam distilled at atmospheric pressure to remove the unreacted monomers and the latex coagulated with a calcium chloride – acetic acid – ferrous sulphate mixture. The resulting polymer was washed, and dried at 190° F. for 30 min. From 0.2 to 0.4 gm. of the polymer was weighed accurately and added to about 80 ml. of purified benzene. After standing in the dark for 24 hr. the volume was made up to 100 ml. The

solution was filtered through glass wool and the concentration determined by evaporating 20 ml. to dryness and weighing the residue. Per cent gel (benzene insoluble) was calculated. Flow times were determined for the original solutions and for two dilutions with benzene. The following designations were used:

$$\text{Specific flow time } t_{sp} = \frac{t \text{ solution}}{t \text{ benzene}} - 1$$

$$\text{Intrinsic flow time } [t] = \lim_{C \to 0} \frac{t_{sp}}{C}\,.$$

If instead of flow times the kinematic viscosity is used then the extrapolation gives intrinsic viscosity $[\eta]$.

Diluting the vistex mixture with benzene also allowed extrapolation to zero nonsolvent, i.e., gave the true intrinsic viscosity, as shown in Table II.

TABLE II

COMPARISON OF VISCOSITY AND VISTEX VISCOSITY RESULTS

Sample No.	Vistex		Dilute solution viscosity in benzene
	Diluting with benzene/isopropanol mixture	Diluting with benzene alone	
1	2.18	2.85	2.83
2	2.17	2.84	2.88
3	2.20	2.83	2.79
4	2.30	2.96	2.96
5	1.95	2.68	2.54
6	2 25	2.96	2.96

This technique shortened the time for determination of intrinsic viscosity to about one hour and was much more convenient than the usual technique. More detailed studies of vistex (15) and viscosity (4, 32) have been published recently.

The swelling index was the weight of swollen gel divided by the weight of the gel.

An analytical method suitable for the analysis of diisopropyl xanthogen disulphide in latex was highly desirable in order that the rate of disappearance of this compound during the polymerization could be studied. Three methods of analysis for diproxid were tried.

The first method was reduction of diproxid in an alkaline solution with zinc dust and titration of the resulting xanthate with iodine.

Results using this method indicated that the recovery was excellent from pure solutions, varying from 97 to 99%. Recoveries of diproxid from latex varied from 102 to 107%. These recoveries were possible only when the amount of diproxid under analysis was between 10 and 100 mgm., an amount much greater than likely to be met in an analysis of a Buna S-3 latex.

Treatment of diproxid in alcohol solutions with potassium cyanide yields the monosulphide and potassium thiocyanate (3, 31, 41). The latter may be determined either colorimetrically by means of the ferric thiocyanate reaction or by oxidation to the sulphate with excess iodate and back titration of the iodate with thiosulphate.

The Klett-Summerson colorimeter was calibrated with standard potassium thiocyanate solution and with standard solutions of diproxid. For low concentration the results obtained by this method showed an excellent recovery (90 to 100%) and a high degree of reproducibility for amounts greater than 1 mgm.

The third method used the polarograph and was suggested and developed by Kolthoff*.

The arrangement of the polarographic cell is shown in Fig. 1. A Model XII Heyrovsky recording polarograph was used.

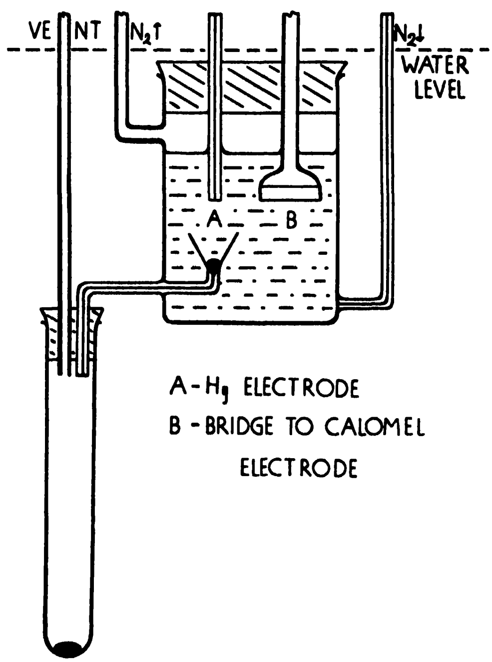


FIG. 1. *Polarograph cell.*

Two samples of diproxid were available, B.F. Goodrich Chemical Company diproxid (recrystallized twice from ethanol, m.p. 57° to 58° C.) and a sample obtained from Germany (recrystallized twice from ethanol, m.p. 57° C.).

Results are shown in Table III. Current readings are in galvanometer scale divisions calculated to the highest sensitivity.

The diffusion current was not directly proportional to the concentration of diproxid, but not sufficiently irregular to render a calibration curve difficult.

* *Private communication through Office of Rubber Reserve.*

TABLE III

POLAROGRAPHIC DATA

Concentration of final solution Molar	Residual current, *IR*	Diffusion current, *ID*		*ID* − *IR*		$\frac{ID - IR}{C}$	
		B.F. Good.	German	B.F. Good.	German	B.F. Good.	German
3 70 × 10^{-4}	86	465	510	379	424	1 02	1 14
1 85 × 10^{-4}	86	255	290	169	204	0 91	1 10
0 74 × 10^{-4}	86	145	160	59	74	0 80	1 00
3 70 × 10^{-5}	86		124		38		1 03
2 59 × 10^{-5}	86		112		26		1 01
1 85 × 10^{-5}	86		110		24		1 30
1 48 × 10^{-5}	86		104		18		1 22
1 11 × 10^{-5}	86		101		15		1 36
0 74 × 10^{-5}	86		95		9		1.21
3 7 × 10^{-6}	86		90		4		1 08

The results also showed that the German diproxid registered up to 1/4 greater diffusion current for the same weight concentration. This can only be interpreted as due to difference in purity of the two compounds. The following analytical data would also indicate a difference in purity of the two samples of diproxid.

	B. F. Goodrich	I. G. Farben.	Calculated
M.p.	57–58 5° C.	57 0° C.	—
Carbon	36.03	35.74	35 56
Hydrogen	5 77	5 46	5 18

However, the two samples were judged to be essentially identical with respect to regulator action as shown later.

Experimental

Diproxid Disappearance

In order to obtain the rate at which diproxid disappeared during the polymerization, 0 4 or 0.5 part of diproxid, all added initially instead of 0.09 part added in three increments, was used. This larger amount was used since none of the analytical methods were sensitive enough for small amounts. Diproxid analyses obtained using the colorimetric procedure outlined above gave the results shown in Fig. 2.

Curves *A* are the time–conversion curves, the upper obtained at 45° C. and the lower at 50° C. The corresponding residual diproxid disappearance curves (*B*) indicate that the rate of disappearance is quite rapid. Only a very small amount remains after 20 to 25% conversion. There is some suggestion that the rate of disappearance is increased by increased temperature (lower curve). If the rate of disappearance is first order these results would be applicable at lower concentrations of diproxid as well.

Comparison of German and American Regulators

Tables IV and V show the polymerization data obtained at 50° C. and at 45° C. Table V also shows a comparison of the I. G. Farbenindustrie and B. F. Goodrich Chemical Company samples of diproxid. No vistex viscosity

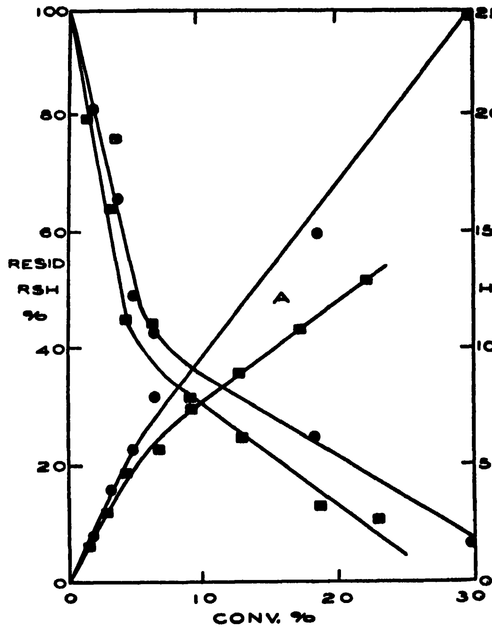


FIG. 2. *Diproxid disappearance in the Buna S-3 system; (A) time–conversion, (B) residual diproxid–conversion.* ● *8 oz. bottle, 3.10 parts Nekal, 1.4 parts* Na_2SO_4*, 45° C.* ■ *32-oz. bottle, 4.00 parts Nekal, 0.7 parts* Na_2SO_4*, 50° C.*

TABLE IV

BUNA S-3 POLYMERIZATION AT 50° C.

(0.09 part of diproxid added in increments of 0.03 part at 13, 30, and 45% conversion)

Time, hr.	Conversion, %	$[t_v]$	$[t]$	Gel, %
5.5	13 2	2.30	4.75	14.4
10.5	25.2	2.30	4.10	25.8
15.75	37.2	2.30	3.60	26.1
22.75	51 0	1.90	2.50	26.4
30.0	65.0	1.30	1.50	55.5

data were determined on this series (Table V) but Table VI shows the vistex results obtained on an identical group. It is evident that the regulating activities are essentially identical. The results are much more consistent when the vistex viscosity is used rather than the dilute solution viscosity. In general, too, the rate of conversion is slow and the viscosity decreases with increasing conversion as the gel increases.

TABLE V

POLYMERIZATION AT 45° C.

(0.09 part of diproxid added in increments of 0.03 part at 13, 30, and 45% conversion)

Time, hr.	Conversion		[t]		Gel	
	German diproxid	Goodrich diproxid	German diproxid	Goodrich diproxid	German diproxid	Goodrich diproxid
5	7.2%	7.2%	4.70	4.25	5.5%	6.0%
13	19.5	20.3	4.85	5.50	17.5	8.0
20	30.6	30.3	3.00	4.70	61.5	11.0
29	41.7	43.7	3.15	2.25	23.0	49.5
34	49.8	49.8	3.80	2.95	9.5	4.0
41	59.2	59.2	2.50	2.70	5.0	35.5

TABLE VI

POLYMERIZATION AT 45° C.

(0.09 part of diproxid added in increments of 0.03 part at 13, 30, and 45% conversion)

Time, hr.	Conversion		$[t_v]$	
	German diproxid	Goodrich diproxid	German diproxid	Goodrich diproxid
8.5	13.6%	13.6%	3.90	3.90
13.0	21.0	22.0	3.20	3.30
20.0	29.0	29.0	2.90	2 95
26.5	39.0	39.5	2.55	2.60
34.0	48.0	51.0	2.20	2.20
41.75	58.0	58.0	1.90	2.10

Polymerization Data

Figs. 3 and 4 and Tables VII and VIII record the polymerization data obtained in investigating the possibility of observing a constant vistex value throughout the reaction. These data were obtained by varying the time and amounts of regulator increments. Fig. 3 gives the data for an unregulated system. Curve *A* is the time–conversion curve and Curve *B* the viscosity–conversion curve. The latter can be seen to reach a peak at about 10% conversion. The former is S-shaped. Fig. 4 gives the data for a system in which various amounts of diproxid were added at 13% conversion, and 0.06% diproxid at 8% conversion; before the peak of the vistex–conversion curve was reached. An additional 0.03% was added at 33% conversion. Of the lower pair, Curve *A* is the time–conversion curve for the first series and Curve *B* for the second experiment. Of the upper pair, Curve *A* is the viscosity–conversion curve for the first series and divides into three branches. Branch 1 resulted from 0.015% diproxid at 13% conversion, branch 2 from 0.030% similarly, and branch 3 from 0.060%. On the other hand, the addition of 0.06% at 8% conversion and 0.03% at 33% conversion resulted

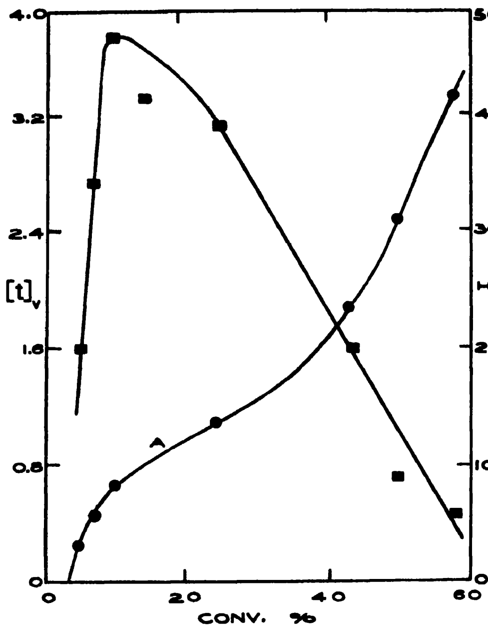


FIG. 3. *Polymerization carried to 60% conversion with no regulator present; (A) time-conversion, (B) viscosity-conversion.*

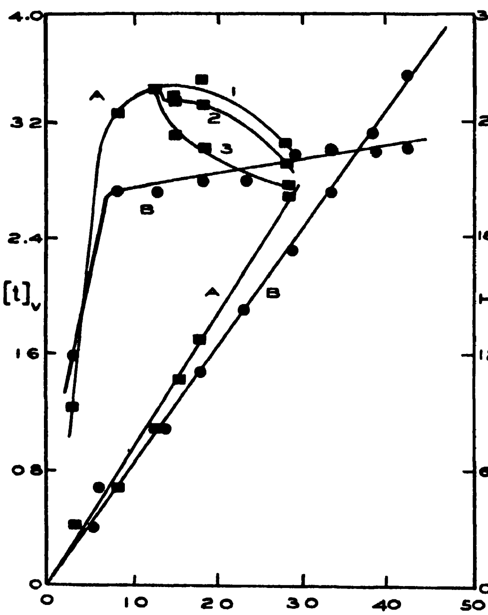


FIG. 4. *Effect of time and amount of diproxid addition. Curves (A) diproxid added at 13% conversion; branch (1) 0.015%; branch (2) 0.030%; branch (3) 0.060%. Curves (B) 0.060% at 8% conversion and 0.030% at 33% conversion. Lower curves, time-conversion; upper, viscosity-conversion.*

in Curve *B*, which is considered reasonably constant although lower than desirable. It can be seen that the viscosity remains quite constant to 42.5% conversion in the latter case.

The latex of the polymers of 38 and 42.5% conversion (Fig. 4, Curve *B*) were divided into two samples each. One-half of each was coagulated with isopropanol and dried *in vacuo* for two hours. The remaining portions of each were coagulated with calcium chloride and acetic acid. Antioxidant was added before coagulation (1.5% BLE based on polymer by weight). The polymers were dried in a hot air oven at 190° F. for 30 min. All polymers showed 100% solubility in benzene. The polymers obtained by coagulation with isopropanol exhibited identical [*t*] values of 4.00 while those coagulated with calcium chloride and acetic acid possessed a lower value of 3.50. These data indicate the high molecular weight of the polymer and the effect of the type of coagulation on the molecular weight of the resultant dry polymer.

In the next three series each sample was an individual 8-oz. charge. The data are collected in Table VII. From these it can be seen that rate of reaction at 45° C. is about 2% conversion per hour. The vistex viscosity using benzene/isopropanol solvent is somewhat lower than the dilute solution viscosity of the same sample, and the vistex viscosity in chlorobenzene/pyridine solvent approximates the dilute solution viscosity. The dilute solution viscosity–conversion curves are not as horizontal as desired. The gel content of the coagulated sample was not consistent but was low usually.

The polymers for viscosity studies coagulated by the special alcohol technique were treated under as nearly as possible air-free conditions. The stopped but unstabilized latex was released into ethanol through which nitrogen had been bubbled, and the syringe weighed before and after in order to obtain the exact weight of polymer transferred. The nitrogen was bubbled through until the rubber had been thoroughly washed, the ethanol was drained off, the tube closed with a glass stopper and the sample dried by evacuation of the chamber at room temperature. As soon as the sample was dry it was removed from the screen and added directly to benzene. A check on the subsequent concentration of rubber in the benzene solution indicated no appreciable loss of material.

When the polymerization was carried out in 32-oz. bottles the samples represented small amounts withdrawn by syringe. The data are in Table VIII. Most of the final samples were stabilized with three parts of phenyl-β-naphthylamine added as an emulsion or in styrene solution, and were coagulated with calcium chloride – acetic acid – ferrous sulphate coagulant, and the Mooney was determined. Half of the sample was then heat softened in a Dietert Moisture Tester at 140° C. for 90 min. and the Mooney determined again as was also the gel, dilute solution viscosity, and swelling index. These results are in Table IX and include similar data for a sample of German Buna S-3. The calculated intrinsic viscosities were based upon the work of Back (1) from which the results for natural rubber are quoted.

TABLE VII

POLYMERIZATION DATA

Sample No.	Time, hr.	Conv., %	Vistex		[t]	Gel, %	Comment
			Chloro/ pyridine	Benzene/ isoprop.			
A. Diproxid: 0 06 at 6% conv , 0 03 at 45 5% conv., 45° C.							
0	0.0	0 0	0 00	0 00	0.00	0 0	Hydroquinone (HQ 0 17/100 mon.
1	4 0	4 7	5 35	3 85	4 35	0 0	BLE 1 5/100 rubber
2	8 0	14 2	3 25	2 95	3 00	0 0	
3	12 1	25 2	3 00	2 75	3 10	0 0	1–3 Brine-acid coag.
4	16 0	34 1	4 00	3 40	3 60	2 0	4-8 $CaCl_2$–HOAc coag.
5	19 9	42 9	4 05	3 60	4 40	7 0	
6	24 0	50 2	—	3 40	3 05	30 0	
7	28 0	59 7	2 65	2 60	2 40	42 0	
8	33 5	68 3	2 20	2 35	1 55	65 5	
B Diproxid· 0 06 at 10 8% conv., 0 03 at 38 9% conv , 45° C.							
0	0 0	0 0		0 00	0 00	0 0	HQ 0 17/100 mon.
1	3 0	5 3		6 00	3 60	0 0	BLE 1 5/100 rubber
2	6 0	12 2		3 95	3 60	2 5	
3	9 5	20 4		4 30	4 75	9 0	1–6 $CaCl_2$–HOAc coag.
4	12 0	24 6		3 55	4 30	10 0	
5	15 0	33 6		3 70	4 40	8 0	
6	18 0	40 2		3 60	4 40	7 5	7–8 Isopropanol coag.
7	21 0	49 0		3 55	4 30	2 0	
8	24 0	56 7		3 10	3 05	57 5	
C. Diproxid: 0 03 at 0 0, 12 8, and 24 4% conv., 45° C							
0	0 0	0 0		0 00	0 00	0 0	HQ 0 17/100 mon.
1	3 0	3 0		2 00	1 50	0 0	Coag. and dried by special technique and placed directly in benzene
2	6 0	7 3		3 65	2 15	0 0	
3	9 0	11 3		2 50	2 35	0 0	
4	12 0	13 4		2 60	2 15	0 0	
5	15 0	9 3		3 25	2 10	0 0	
6	18 0	24 1		2 60	2 60	0 0	
7	21 0	28 8		2 45	2 65	0 0	
8	24 0	40 0		2 90	3 15	0 0	

It can be seen that as the experiments proceed (Table VIII) the viscosity–conversion curves become quite horizontal. In some cases there is considerable gel but this is very loose. In one sample the gel dropped from 90% to 30% upon massing the sample for Mooney determination. The ratio of $[\eta]/[\eta_v]$ is about 1.3.

The ratio of the heat softened Mooney to the original Mooney is noted to be quite constant for high Mooney polymers in proportion. The high Mooney

TABLE VIII

Polymerization data

Sample No.	Time, hr.	Conv. %	$[t_v]$	$[t]$	Gel, %	Swelling index	$[t]/[t_v]$
A. Diproxid: 0.03 at 2.7 and 14.8% conv., 0.06 at 24.3% conv., 50° C.							
0	0.0	0.0	0.00	0.00	0.0		—
1	2.0	2.7	1.75	4.20	85.5		2.40
2	4.0	5.4	2.05	3.05	55.0		1.49
3	6.0	9.0	2.00	3.10	30.0		1.55
4	8.5	14.8	1.95	3.10	18.0		1.59
5	10.0	16.5	2.05	3.05	12.0		1.49
6	12.0	21.8	2.00	2.65	12.0		1.32
7	13.0	24.3	2.05	2.55	16.5		1.24
8	23.5	41.4	1.25	2.05	10.0		1.64
(Note: *Intrinsic flow time not corrected for nonpolymer solids to this point, all values corrected hereafter, also intrinsic viscosity and intrinsic vistex viscosity used hereafter.*)							
B. Diproxid: none, 50° C.							
			$[\eta_v]$	$[\eta]$			$[\eta]/[\eta_v]$
1	2.5	3.7	6.50	8.90	38.5		1.37
2	4.5	6.6	8.85	9.05	45.5		1.02
3	6.5	12.7	7.20	9.95	12.0		1.38
4	8.0	17.1	6.65	6.30	74.5		0.95
5	9.5	19.0	6.35	6.40	63.5		1.01
6	11.0	21.7	5.50	6.15	69.0		1.12
7	12.5	27.0	5.00	6.60	20.5		1.32
8	24.0	53.7	1.85	5.15	89.0		2.79
C. Diproxid: 0.03 at 0.0, 18.5, and 35% conv., 45° C.							
1	6.5	8.2	3.75	5.15	11.0	98.0	1.38
2	8.5	11.4	3.35	4.50	8.0	43.0	1.34
3	10.5	15.3	3.45	4 35	2 5	39.0	1.26
4	12.5	18.3	3.65	4.65	1.0	145.0	1.27
5	30.5	40.8	3.95	6.30	19.5	62.0	1.59
6	32.5	43.2	4.10	5.25	29.5	118.0	1 28
7	35.5	48.2	4.20	3.70	84.5	54.0	0 88
8	41.0	53.5	3.05	4.05	79.5	51.5	1.32
D. Diproxid: 0.04 at 0, 18.0, and 30.5% conv., 45° C.							
1	9.0	14.2	2.90	3.95	0 0		1.36
2	12.5	22.5	2.85	3.70	0.0		1.30
3	16.0	27.7	2.80	3.40	0 0		1.21
7	21.5	30.5	2.80	3.40	0.0		1.21
8	27.5	39.3	2.75	3.25	0.0		1.18
4	33.0	50.4	2.90	3.65	0.0		1.26
5	36.0	54.3	2.95	3.90	0.0		1.13
6	39.5	57.2	3.25	3.75	41.0	85.0	1.15

TABLE VIII—*Concluded*

POLYMERIZATION DATA—*Concluded*

Sample No.	Time, hr.	Conv %	$[\eta_o]$	$[\eta]$	Gel, %	Swelling index	$[\eta]/[\eta_o]$
E. Diproxid: 0 05 at 0, 14 8, and 28 6% conv , 45° C.							
1	9 2	13 4	2 50	3 25	0 0		1 30
2	12 3	18 3	2 50	3 70	0 0		1.47
3	15 8	23 9	2 50	3 15	0 0		1.26
7	26 0	28 6	2 45	2 60	0 0		1 06
8	29 6	32 8	2 15	2 30	0 0		1 07
4	33 2	46 8	2 75	3 55	0 0		1 29
5	36 4	50 7	3 05	3 90	0 0		1 28
6	40 3	54 9	3 30	4 25	0 0		1 29
F. Diproxid: 0 06 at 0, 23 8, and 42 4% conv., 45° C , 4 0 parts Nekal, no Na_2SO_4							
1	10 2	14 9	2 28	2 88	0 0		1 26
2	13 4	23 8	2 40	3 07	0 0		1 28
3	16 8	29 9	2 39	2 97	0 0		1 24
4	34 2	67 5	3 49	4 77	70 0	21 0	1 36
5	36 2	71 1	2 93	3 81	89 5	30 5	1 30
6	37 2	73 4	2 69	3 50	91 0	51 5	1 30
G. Diproxid· 0 06 at 0 0, 19 3, and 43 9% conv , 50° C , 4 0 parts Nekal, no Na_2SO_4							
1	6 2	13 0	1 90	2 45	0 0		1 29
2	8 4	19 3	2 29	2 94	0 0		1 28
3	12 0	30 2	2 29	2 92	0 0		1 27
4	15 0	43 9	2 29	2 98	0 0		1 30
5	17 4	50 7	2 58	3 47	0 0		1 35
6	19 6	58 7	2 80	3 65	1 0	4 80	1 30
H. Diproxid: 0 07 at 0, 23 4, and 38 7% conv , 50° C , 4 0 parts Nekal, no Na_2SO_4							
1	6 2	21 4	2 72	3 18	33 5	107 0	1 17
2	7 0	23 4	2 85	3 75	27 5	81 0	1 32
3	9 0	28 0	2 58	3 54	2 5	200	1 37
4	12 6	38 7	2 42	3 05	0 0		1 26
5	16 6	47 0	2 20	2 99	0 0		1 36
6	20 0	52 2	2 20	2 74	0 0		1 25
I. Diproxid· 0 07 at 0, 22 8, and 40 3% conv , 50° C , 4 0 parts Nekal, no Na_2SO_4							
1	6 2	19 6	2 18	2 83	0 0		1 30
2	8 4	26 1	2 17	2 88	0 0		1 33
3	10 8	33 8	2 20	2 79	0 0		1 27
4	12 8	40 3	2 30	2 96	0 0		1 29
5	15 4	46 5	1 95	2 54	0 0		1 30
6	20 0	58 8	2 25	2 96	0 0		1 32

(All polymers coagulated as indicated in Table VII, Part C)

TABLE IX

HEAT SOFTENING OF POLYMERS

Sample No (Table VIII)	Conv, %	$ML/4'$	$\frac{ML/4'\text{HS}}{ML/4'\text{orig}}$	Gel, %	Swelling index	$[\eta]_{obs}$	$[\eta]_{calc}$ *	$\frac{[\eta]_{obs}}{[\eta]_{calc}}$
VIII B original	53 7	155 5	0 460	31 5	93 5	2 85	4 38	0 650
Heat soft	—	71 5	—	0 0	—	2 02	—	—
VIII C original	53 5	168 5	0 425	62 5	73 0	3 37	4 67	0 722
Heat soft	—	71 5	—	10 5	134 5	2 17	2 54	0 854
VIII D original	57 2	121 5	0 415	0 0	—	3 45	—	—
Heat soft	—	50 5	—	2 0	360	2 01	2 08	0 967
Original	39 3	95 5	—	0 0	—	4 03	—	—
VIII E original	54 9	120 0	0 415	0 0	—	3 51	—	—
Heat soft	—	49 5	—	0 0	—	2 15	—	—
VIII F 1 original	37 8	136 5	—	0 0	—	4 16	—	—
F 2 heat soft	73 4	71 5	—	32 0	70 0	1 56	2 54	0 613
VIII G original	58 7	99 0	0 651	0 0	—	3 14	—	—
Heat soft	—	64 5	—	1 5	570	1 99	2 38	0 837
VIII-H original	52 2	64 5	0 783	0 0	—	2 38	—	—
Heat soft	—	50 5	—	0 0	—	2 10	—	—
VIII I original	58 8	90 5	0 675	0 0	—	2 56	—	—
Heat soft	—	61 0	—	0 0	—	2 29	—	—
Natural rubber	—	100 0	—	35 5	—	5 35	1 85	2 90
I G Farben Buna S-3								
Original	—	149 5	0 415	4 5	—	3 35	4 24	0 790
Heat soft	—	62 0	—	4 0	—	2 20	2 33	0 946

* $[\eta]_{calc} = 0\ 0219\ ML/4' + 0\ 97$, $[\eta]$ *that would be obtained if the polymer were gel free.*

copolymers heat softened at a rate comparable to that of I. G. Farbenindustrie Buna S-3. The ratio of $[\eta]_{obs}/[\eta]_{calc}$ did not differ much from that for GR–S, nor approach that of natural rubber.

While a horizontal intrinsic viscosity – conversion curve was obtained in the 32-oz. bottle polymerizations by adding 0.070 part of diproxid at 0, and approximately 20, and 40% conversion the intrinsic viscosity and the Mooney plasticity were both lower than those of I. G. Farbenindustrie Buna S-3. The copolymer produced using 0 180 part of diproxid had an intrinsic viscosity increasing at the end of the reaction; no combination using 0.100 parts of diproxid would give the desired gel-free polymer with a horizontal intrinsic viscosity – conversion curve. It is probably very difficult, if not impossible, to duplicate exactly a copolymer manufactured on a plant scale in bottle reactors; the agitation conditions are different.

Regulating Index of Diproxid and Mercaptans

Since the significant difference between Buna S-3 and GR–S lies in the regulator and its mode of addition, it was of prime importance to compare

its effectiveness as a regulator with that of normal and tertiary mercaptans. This was done by measuring (26) the residual mercaptan at various conversions. The data are collected in Fig. 5 and should be compared with the data in Fig. 2.

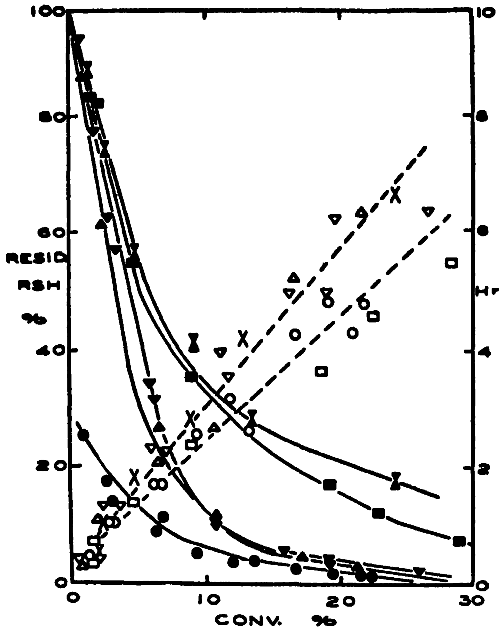


FIG. 5. *Residual mercaptan in Buna S-3 system. Open points, time–conversion; broken lines, representative curve; upper, for normal mercaptans, lower, for tertiary mercaptans. Solid points, residual mercaptan – conversion.* ● *Tertiary butyl 0.2,* ■ *tertiary amyl 0.2,* ▲ *n-decyl, 0.4,* ▼ *n-dodecyl, 0.4,* ⧗ *n-tetradecyl 0.4.*

The time–conversion curves, broken lines, indicate somewhat greater rates of reactions with tertiary mercaptans (lower curve) than with normal mercaptans (upper curve). The solid curves, residual mercaptan – conversion curves, would appear in all cases, except with tertiary butyl mercaptan, to be similar to that for diproxid.

However the activity of the mercaptan is better expressed as regulating index, defined as

$$r = \frac{d \ln R}{dP},$$

in which R is the per cent residual regulator at fractional conversion P, and was found by plotting $\ln R$ against P. Extrapolating the initial straight line portion of the resulting graph to zero conversion gave the waste factor defined as the difference between 100 and the intercept. The data are summarized in Table X, including previously published results obtained using the GR–S system (5, 30). The waste factor arises, presumably, from disappearance of mercaptan in side reactions such as disulphide formation.

It is evident that tertiary amyl mercaptan approximates diproxid in its regulating characteristics and that diproxid lies between normal dodecyl and

TABLE X

REGULATING INDEX AND WASTE FACTOR FOR DIPROXID AND MERCAPTANS

Regulator	Regulating index	Waste factor	Reference
In Buna S-3 system			
Diproxid	14.7	0	
tert. butyl mercaptan	16.1, 15.1	0.76, 0.70	
tert. amyl mercaptan	12.9, 12.9	0.0, 0.0	
n-decyl mercaptan	20.0	0.0	
n-dodecyl mercaptan	20.0, 20.0	0.0, 0.0	
n-tetradecyl mercaptan	11.9	0.0	
By Mutual formula			
n-octyl mercaptan	11.0	0.73	5
n-decyl mercaptan	8.5	0.51	5
n-dodecyl mercaptan	2.50	0.0	5
tert. butyl mercaptan	2.35	0.10	5
tert. decyl mercaptan	3.85, 13.7	0.0, 0 64	5, 26
tert. octyl mercaptan	2.80, 3.95	0.0, 0.33	5, 26
tert. dodecyl mercaptan	3.16	0.045	26
tert. hexadecyl mercaptan	0.58	0.0	26

normal tetradecyl mercaptan in its regulating characteristics. Particularly noticeable is the difference in the regulating index for the same mercaptans in the Buna S-3 and GR–S systems. The index is much lower in the latter case.

Use of Mercaptans in Buna S-3 Formula

Polymerization data using tertiary butyl mercaptan are given in Fig. 6 and using tertiary amyl mercaptan, in Fig. 7. These results are quite comparable to those obtained using diproxid. Data obtained when normal mercaptans are used are given in Table XI. Curves *A* of Fig. 6 show the time–conversion curves. The upper of pair *B* indicates the decline in viscosity after 14% conversion, regardless of the amount of mercaptan added. On the other hand, Curve *B* shows a rising viscosity when 0.06% tertiary butyl mercaptan was added at 8% conversion. The ideal must be somewhere between the two values. Better results were obtained with tertiary amyl mercaptan, Fig. 7. Table XI indicates the unsatisfactory use of *n*-octyl mercaptan but encouraging use of *n*-decyl mercaptan.

Heterogeneity of the Molecular Weights

An approximation to the molecular weight distribution may be determined from the viscosity average molecular weight (M_v) and the number average

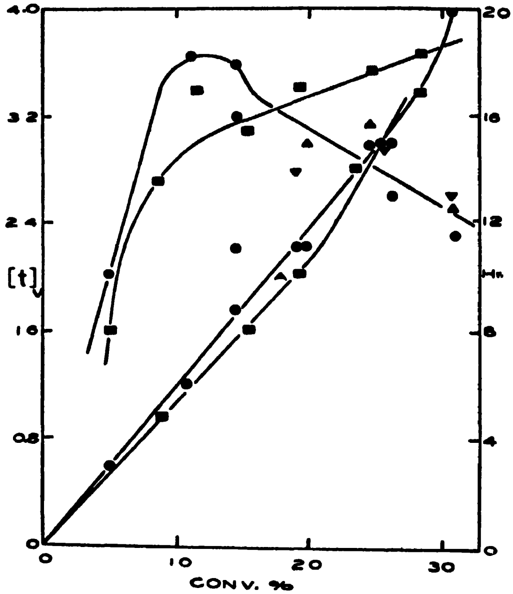


FIG. 6. *Tertiary butyl mercaptan in the Buna S-3 system; (A) time-conversion curves, (B) viscosity-conversion curves.* ● *Mercaptan added at 14% conversion,* ● *0.015%,* ▲ *0.030%,* ▼ *0.060%;* ■ *0.060% added at 8% conversion.*

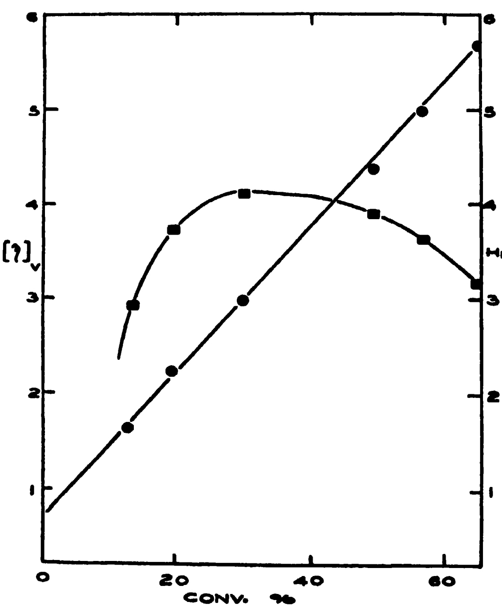


FIG. 7. *Polymerization data using 0.009 parts t-amyl mercaptan at 0, 19, and 49% conversion.* ● *Time-conversion,* ■ *viscosity-conversion.*

TABLE XI

POLYMERIZATION DATA USING NORMAL MERCAPTANS

Time, hr.	Conversion, %	Intrinsic viscosity	Residual mercaptan
n-Octyl mercaptan. 0.06 part at 0, 31, and 47% conv.			
5.2	25.4	4.65	66.9%
6.4	30.9	5.20	66.7
7.6	38.8	4.59	36.7
8.6	47.1	4.00	34.0
10.0	57.5	3.54	1.4
n-Octyl mercaptan. 0.097 part at 0, 19, and 41% conv.			
2.0	6.8	0.55	68.2
4.2	18.6	1.59	66.9
6.2	31.4	1.57	33.9
7.6	40.8	2.22	33.1
9.4	55.1	2.22	0
10.2	62.3	2.74	0
	Final Mooney 46 *ML*/4′		
n-Decyl mercaptan. 0.05 part at 0, 22, and 41% conv.			
2.4	11.2	7.51	67.2
4.2	21.6	3.30	67.2
5.6	30.6	2.90	38.4
7.0	41.4	3.68	38.4
8.0	48 7	3.67	37.7
9.3	57.9	3.68	1.0
	Final Mooney 93.0 *ML*/4′		

by the logarithmic number distribution (Maxwellian type with unlimited range toward infinite molecular weight).

$$dn = \frac{Ne^{-y^2}dy}{\sqrt{\pi}}$$

where $y = \dfrac{1}{\beta} \ln \dfrac{M_v}{M_0}$;

dn = number of molecules in the interval y to $y + dy$;

N = total number of molecules;

β = degree of heterogeneity, and is zero for a homogeneous polymer;

M_0 = molecular weight at which the peak occurs in the distribution curve.

From the above relations it may be derived for butadiene/styrene copolymers that:

$$\beta = 2.35 \log R, \text{ where } R = \frac{\overline{M}_v}{\overline{M}_n}, \text{ and } M_0 = \overline{M}_v.\ R^{-0.598}$$

$\bar{M}_v$ may be determined from the intrinsic viscosity determination and $\bar{M}_n$ from the regulator disappearance curve, assuming that one molecule of regulator is used up per copolymer molecule formed. Assuming that a Buna S-3 sample of 60% conversion with intrinsic viscosity of 3.00 is produced in plant reactors by adding 0.03 part of diproxid at 0, 20, and 40% conversion, the values of β and M_0 will be 1.41 and 11.7×10^4 respectively. Other representative data are in Table XII. The polymers produced in the Buna S-3 system with diproxid would seem to be of more uniform and of higher molecular weight than those produced in the same recipe with normal mercaptans or those produced in the GR–S system.

TABLE XII

HETEROGENEITY OF MOLECULAR WEIGHTS

Polymer	Conv., %	$\bar{M}_v$	$\bar{M}_n$	R	β	$\bar{M}_0$
Diproxid 0.06 at 0 and 0.04 at 40% conversion	10	22.1×10^4	6.06×10^4	3.35	1.70	3.20×10^4
	20	41.5	10.60	3.90	1.81	4.69
	30	68.1	14.40	4.75	1.93	5.68
	40	97.7	18.38	5.30	2.00	6.73
Diproxid 0.06 at 0 and 19 and 0.03 at 38% conversion	10	27.6	6.60	4.20	1.85	2.80
	20	40.4	9.65	4.20	1.85	4.09
	30	40.4	8.25	4.90	1.95	3.18
	40	40.4	9.15	4.40	1.89	3.77
	50	40.6	9.75	4.15	1.85	4.14
	60	64.8	11.15	5.80	2.06	3.80
n-Octyl mercaptan 0.06 at 0, 31, and 47% conversion	20	70.0	5.10	13.70	2.50	10.60
	30	97.7	7.75	13.30	2.49	15.60
n-Octyl mercaptan 0.097 at 0, 19, and 41% conversion	10	6.6	1.55	4.25	1.86	0.66
	20	16.7	1.90	8.70	2.28	0.53
	30	16.7	2.30	7.20	2.17	0.7
	40	26.5	3.05	8.70	2.28	0.63
	50	28.1	2.60	10.90	2.36	0.64
	60	34.0	3.05	11.20	2.36	0.76
n-Decyl mercaptan 0.05 at 0, 22, and 41% conversion	10	13.2	3.60	3.70	1.77	1.64
	20	36.7	7.10	5.15	1.98	2.66
	30	41.5	5.75	7.20	2.18	1.77
	40	54.6	7.05	7.75	2.22	2.07
	50	59.4	6.15	9.65	2.34	1.58
	60	54.4	7.05	8.45	2.26	1.96
n-Dodecyl mercaptan in Mutual formula, 0.5 at 0 conv.	20	3.6	1.8	—	1.30	1.19
	38	9.3	2.4	—	1.81	1.05
	59	15.4	3.1	—	1.97	1.22
	82	32.2	4.0	—	2.24	1.14
Buna S-3, 0.06 diproxid at 0, 20, and 40% conv., constant $[\eta] = 3.00$	60	43.7	9.60	4.55	1.91	2.51

Discussion

It is seen that diproxid is a reactive regulator. At 30% conversion only 6% of the initial amount remained. In regard to our present theories of modification (6, 7, 8, 12, 13, 27, 28, 30, 37, 38, 39, 40) in the emulsion polymerization system this would indicate that increment addition of such a regulator is a necessity if a constant viscosity is to be obtained throughout the reaction.

The rate of polymerization was found to be very sensitive to changes in temperature. A reduction in temperature from 50° C. to 45° C. resulted in a rate decrease from about 2.4% per hour at the higher temperature to about 1.5% per hour at the lower. The significant feature is that this reaction proceeds at a steady rate in the complete absence of a promoter or chain transfer agent. Diproxid is not a promoter, and may indeed be a retarder, particularly in the presence of impurities.

The Buna S-3 polymerization system, although fairly reproducible with regard to conversion is nonreproducible when considering such properties as intrinsic flow time and gel content. However, it is very difficult to see why such anomalies should occur in the polymerization reaction. It is believed that such irreproducible properties might result during the handling of the polymer, i.e., during removal of excess monomers, coagulation of the latex, and drying of the polymer.

Because of the irreproducibility of intrinsic flow time and percentage gel measurements, these methods of characterization were discontinued early in favor of the vistex technique, by which the polymerization reaction may be studied and the "whole" polymer, including soluble and gelled portions, evaluated without the changes brought about during removal of the residual monomers, coagulation of the latex, and drying. By this technique the latex particle is individually dispersed in a mixed solvent system. This results in complete solution or dispersion of both soluble polymer and gel. From the theories of viscosity it is evident that the formation of gel during polymerization will result in an over-all decrease in intrinsic viscosity when the whole-polymer is considered. The complicating feature is that low vistex values may also be obtained with low molecular weight "linear" polymers. Hence, with present methods it is very difficult, in an examination of a vistex–conversion curve, to determine how much of the decrease can be attributed to gel formation and how much to regulation.

From an examination of the data in Fig. 3, which represents the polymerization reaction free from the complications of modification, it is seen that there is a rapid rise in the vistex viscosity from 0 to 13% conversion. This is probably indicative of the formation of polymer molecules of increasing molecule weight and comparatively linear in nature. At about 13% conversion, gel formation begins, owing to branching, cross linking, and increasing molecular weight of the polymer. This results in a continuous falling-off of the vistex to a very low value at the completion of the reaction. Fig. 4 (Curve *A*) shows the same trends except that the formation of gel and consequently

the decrease in vistex is made less pronounced by the addition of regulator after the vistex has reached a maximum value. Fig. 4, Curve *B*, shows a different trend. The results indicate a polymerization in which a constant and fairly high vistex value with increasing conversion was obtained. As was predicted, the polymer produced in this case was entirely free of microgel, as evidenced by the nonexistence of macrogel in the coagulated and dried polymer.

The more comprehensive data in Tables VII and VIII indicate that when corrections are applied for nonrubber constituents it is not easy to obtain a satisfactorily flat vistex viscosity – conversion curve with the smaller amounts of regulator. Indeed best results are obtained with amounts of diproxid of the order of 0.2 part total. The same general trends may be noted with higher diproxid charges as are noted in the preparation of GR–S. The peak of the intrinsic viscosity – conversion curve shifts to higher conversions and the entire curve towards lower viscosities. Increasing the Nekal BX charge increases the rate somewhat and decreases the amount of precoagulum slightly.

The ratio of intrinsic viscosity to intrinsic vistex viscosity varies with the intrinsic vistex viscosity somewhat but was generally rather constant for gel-free samples and could be represented by the equation:

$$[\eta] = 0.175\,[\eta_v]^2 + 0.92\,[\eta_v]$$

Comparative data taken from smoothed-out viscosity conversion and vistex conversion curves are given in Table XIII. Also it was found, following the

TABLE XIII

RATIO OF INTRINSIC VISCOSITY TO VISTEX VISCOSITY

Sample No.	$[\eta]$	$[\eta_v]$	$[\eta]/[\eta_v]$
1	2.45	1 90	1.29
2	2.95	2.30	1.28
3	2.95	2.30	1.28
4	2.95	2.30	1.28
5	3.24	2.54	1.28
6	3.48	2.74	1.27
7	3.42	2.54	1.37
8	3.07	2.30	1.33
9	2.84	2.18	1.30
10	2.85	2.19	1.30
11	2.85	2.20	1.30
12	2.85	2.20	1.30
13	2.87	2.19	1.30

work of Back (1), that $[\eta] = 0.0219 \times ML/4' + 0.97$ for gel-free copolymers, and $[\eta] = (0.0219ML/4' + 0.97) \times (0.93 - 0.0093\text{ gel})$ for gel-containing polymers. The intrinsic viscosity and the gel were determined on the sample after they were massed for the Mooney determination. This equation differs but slightly from that found by Back for GR–S and is subject to the same limitations.

The regulating indices of mercaptans would seem to be higher in the Buna S-3 system than in the Mutual formula. Of the commonly available materials only tertiary amyl mercaptan would seem to fulfill the conditions of having the same regulating index and the absence of waste factor. Polymer prepared using tertiary amyl mercaptan in amounts corresponding mole for mole to the diproxid should yield the same polymer. This would appear to be true within the ability of the system to discriminate.

However, should the schedule of additions of mercaptan be altered, some other mercaptan would accomplish the same results, the essential requirements being that the activity of the regulator oscillate between two values, both of which are above that which will allow gel formation readily and below that which will result in low molecular weight polymer. These values could be calculated from the data presented in a specific case. It is evident, too, why the use of *n*-dodecyl mercaptan in place of diproxid would lead to the formation of a more heterogeneous polymer when the same schedule of addition was adhered to; the dodecyl mercaptan should be added in smaller molar quantities and more often. The main advantage in replacing diproxid by a mercaptan is the very considerable increase in the rate of the reaction, and the system seems to be more reproducible. The effect of the mercaptans on rate may be arranged in the order tertiary amyl > tertiary butyl > *n*-tetradecyl and *n*-dodecyl > *n*-decyl.

Through trial and error the scientists at I. G. Farbenindustrie had arrived at a schedule of addition of diproxid which gave them a rather homogeneous polymer of just about the maximal molecular weight below where gel forms readily. However, the system is not unique or inexplicable and may indeed be improved upon by using mercaptans. On the other hand, application of the knowledge obtained as to regulating index of diproxid in relation to other mercaptans would enable a similar polymer to be prepared using the Mutual formula if it were desirable. The polymer produced would be very tough and difficult to process as prepared. While such a polymer could be heat softened or degraded to a processing level well within that suitable for current factory techniques, such a step is cumbersome, costly, and, based upon reports from Europe, not easily controlled. Thus, the more suitable approach to an improved general purpose tire rubber would seem to be along the lines of lower polymerization temperatures (17, 35).

Acknowledgment

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PILOT PLANT STUDY OF GERMAN BUNA S-3 CHEMICAL RUBBER[1]

By T. L. Davies[2] and H. Leverne Williams[3]

Abstract

Buna S-3 chemical rubber was prepared in 5 and 110 gal. glass lined autoclaves. The polymerization conditions were not identical with those reported by the Germans or by a concurrent laboratory program. The polymers failed to heat soften in a manner comparable to the German material but, nevertheless, when the polymer was degraded on a mill and compounded in a standard tire tread recipe the resulting vulcanizate had properties superior to GR–S and approximating those of low temperature chemical rubber, although the Buna S-3 lacked the ease of processing of the low temperature copolymer.

Introduction

The German general purpose tire rubber, Buna S-3, although produced in a manner very similar to that used for the production of chemical rubber (GR–S) in Canada did differ both in its method of manufacture and processing. Like GR–S the I. G. Farbenindustrie product was a butadiene–styrene copolymer prepared in emulsion. The catalyst was potassium persulphate, the emulsifier was Nekal BX (isobutylnaphthalene sodium sulphonate) and the regulator or molecular weight controller was diisopropyl xanthogen disulphide (diproxid). A considerable volume of data became available following the visits of several investigators to Germany (1, 2, 3, 4, 7, 8, 9, 10, 11, 14, 15, 16, 17, 19, 20, 22, 23). Data on various copolymers prepared in this system have been published (18).

The polymer was very tough and in practice was heat softened (6) to the desired plasticity before use. In spite of this economic and processing handicap it was of interest to parallel the laboratory investigation of this polymer and the system in which it was prepared (5) by an attempt to produce larger quantities of the Buna S-3 for compounding and testing studies. When polymers produced at lower temperatures (21) were found to equal or exceed Buna S-3 in properties and were very much easier to process, the Buna S-3 program was terminated. Thus, certain questions remain unanswered by this report, which is intended to define the status of the study upon closing.

Techniques

The criterion for similarity to the I. G. Farbenindustrie product was to produce a polymer of high Mooney plasticity by the increment addition

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[2] *Supervisor, No. 1 Pilot Plant.*

[3] *Research Chemist, Physical Chemistry Research Laboratory.*

of diproxid regulator to maintain a horizontal intrinsic viscosity–conversion relation up to 60% conversion of hydrocarbons to copolymer.

The polymers were milled on a standard laboratory rubber mill and compounded in the standard test recipe for tire tread stocks. Unless otherwise indicated, the test methods on the vulcanizates conformed with those in use in standard testing laboratories.

Viscosities, gel, and other molecular weight data were obtained as in the previous report (5).

Experimental

Polymerization and Characterization of Polymers

Table I shows the polymerization data obtained on a large number of Buna S-3 charges in the 5-gal. reactors at 45° C.

TABLE I

POLYMERIZATION DATA

Polymer	Time hr	Diproxid	Conv , %	[t]	Gel, %	[t_s]	Mooney	Coagulation
T 199 4	0	0 033	0		0			
			8 5	1.7	0			
			18	2 7	0			
		0 033	25 5	3 3	0			
			31 5	3 7	0			
			37 5	3 7	0			
		0 033	44 5	4 5	5			
			53 0	0 95	78			
	32 5		56 5	2 4	63		150 L	NaCl, H_2SO_4
T-443 80	0	0 033	0					
		0 033	20	1 00	80 25			
		0 033	40	1 25	83 25			
	30 3		61 2	3 95	8 0		90 S	Alum
T-445 4	0	0 047	0					
		0 047	20	1 73	76 5			
		0 047	40	0 25	79 0			
	52 5		61 2	1 46	70 5		83 S	NaCl, H_2SO_4
T-446 1	0	0 047	0					
		0 047	20	2 75	0			
		0 047	40					
	33		60 7	4 57	7 0		95 S	Alum
T-472 3	0	0 049	0					
		0 035	20	0 55	60 8			
		0 056	40	0 68	52 2			
	33 8		69 5	1 00	68 8		88 S	Alum
T-493-2	0	0 035	0					
		0 049	20	3 05	0 75			
		0 056	40	4 7	2 5			
	30 5		59 5	2 95	12		88 S	Alum
T-525 1		0 033	20		85 0	3.5		
		0 033	40		80 8			
		0 033	60					
	48		80 8		76 5		97 S	Alum

L, Large Rotor ML/4′; S, Small Rotor MS/4′.

TABLE I—*Continued*

POLYMERIZATION DATA—*Continued*

Polymer	Time, hr.	Diproxid	Conv., %	$[\eta]$	Gel, %	$[\eta_g]$	Mooney	Coagulation
T-526-2		0.033	20		81.1	1.92		
		0.033	40		94.5	2.00		
		0.033	60		97.4	0.71		
	42.5		77		95.6	0.93	108 S	Alum
T-540-1		0.035	20		62.3	1.0		
		0.025	40		74.5	1.55		
		0.040	60					
	64.6		79.7		78.0	0.80	103 S	Alum
						0.43		
T-541-3		0.035	20		34.2			
		0.025	40		24.8	0.365		
		0.040	60					
	39.2		79		7.0	0.49	116 S	Alum
T-559-1		0.033	0					
		0.033	20					
		0.033	40					
	22.5		62.0				76 S	Alum, $FeSO_4$
T 560-1	0	0.03	0					
		0.03	20		0	2.41		
		0.03	40		8.5	3.15		
	45		51.0		8.4	2.82	90.5 S	Alum, $FeSO_4$
T-589-1	0	0.033	0					
		0.033	20		42.5	2.58		
		0.033	40		82.5	3.05		
	51		61		77.5	2.65	88 S	See Table III
T-576-1	0	0.033	0					
		0.033	20			2.10		
		0.033	40					
	48		61.8			2.24	85 S	Alum, $FeSO_4$
T-593-2	0	0.1	0					
			20		66.1	1.17		
			40		66.8	1.90		
	28		61.2		72.3	1.30	89 S	$CaCl_2$, HOAc, $FeSO_4$
T-594-2	0	0.14	0					
			20		2.5	0.67		
			40		2.5	2.35		
	33.3		60.8		65.3	1.90	70.5 S	$CaCl_2$, HOAc, $FeSO_4$
T-726-2		0.06	8			1.89		
			33			2.95		
			50			2.77		
	27		60.0			2.32	82 S	CaCl, H_2SO_4, $FeSO_4$
T-730-2		0.04	8			2.95		
		•	20			2.80		
			33			3.20		
			50			3.15		
	30.6		59			2.35	78 S	NaCl, H_2SO_4, $FeSO_4$
T-746-2		0.04	8			3.19		
			20			3.19		
			33			3.12		
		0.02	50			2.85		
	26		59.8			3.20		$FeSO_4$

L, Large Rotor ML/4'; S, Small Rotor MS/4'.

TABLE I—*Concluded*

POLYMERIZATION DATA—*Concluded*

Polymer	Time, hr.	Diproxid	Conv., %	$[t]$	Gel, %	$[t_s]$	Mooney	Coagulation
T-750-2		0 04	8			4.50		
			20			3.17		
			33			3.48		
		0.03	50			2.87		
	36		60 8			2.10	78.5 S	NaCl, H_2SO_4, $FeSO_4$
T-762-2		0.04	8			1.95		
			20			2.05		
			33			3.10		
		0 03	50			3.00		
	28 7		60.7			2.45	60.7 S	$FeSO_4$, NaCl, H_2SO_4

L, Large Rotor ML/4′; S, Small Rotor MS/4′.

It will be noted that the time and amount of diproxid increments were varied in an attempt to obtain a horizontal viscosity and/or vistex versus conversion curve. This was not accomplished but was being approached (see polymer T-746-2). An examination of the results in Table I indicates that a satisfactory degree of reproducibility of the Buna S-3 system with regard to conversion rate, intrinsic flow time, vistex, and Mooney has not been obtained in the Pilot Plant reactors.

The lack of reproducibility makes it difficult to evaluate the effect of varying the amount of diproxid and the time of the addition.

Polymers T-525-1, T-526-2, T-540-1, and T-541-3 were higher conversion polymers than regular Buna S-3 and Polymer T-560-1 was prepared to 50% conversion.

Heat Softening

In these experiments the polymers were placed in a hot air oven at 250° to 260° F. for a period of several hours. Samples were removed at intervals for Mooney determination. The results are shown in Table II.

Examination of the data shows that the rate of Mooney decrease for the heat softening of polymers prepared here was much lower than that of the German Buna S-3, even when the sample contained iron as catalyst. The extremely low rate of heat softening of polymers T-443-80 and T-559-1 may be attributed to the use of alum to coagulate the latex. However, variation of the coagulation system for Pilot Plant polymers has not yet produced rates of heat softening approaching that of German Buna S-3. The effect of different types of coagulation on heat softening is shown in Table III for polymer T-589-1 and at a temperature of 260° F. for a period of 30 min.

It is to be observed that coagulation with sodium chloride – sulphuric acid – ferrous sulphate mixture gave a polymer that showed a greater Mooney decrease on softening. Another important feature shown by these results is the variation in the Mooney and gel caused by different types of coagulation.

TABLE II

HEAT SOFTENING DATA

Time	Mooney *ML/4'*		
	T-443-80	*T-559-1	German Buna S-3
15 min.	—	134.5	156.5
30 "	129	136.0	135
45 "	123	—	—
60 "	119, 128	119.5	93.0
80 "	—	121.5	76
90 "	109	—	—
100 "	—	123.0	57.5
2 hr.	105, 109	123.5	51.5
3 "	99, 105	—	—
4 "	101.5	—	—
5 "	98.0	—	—
6 "	101.5	—	—
7 "	99.5	—	—
8 "	104.5	—	—
9 "	109.5	—	—
10 "	105.5	—	—
11 "	107.0	—	—
12 "	110.0	—	—

* *Coagulant for Polymer T-559-1 contained 0.12 gm. $FeSO_4 . 7H_2O$ per 100 gm. of polymer.*

TABLE III

EFFECT OF TYPE OF COAGULATION ON POLYMER

Polymer T-589-1	Coagulation type	Original gel, %	Original Mooney *ML/4'*	Final Mooney *ML/4'*
A	Alum	78.8	149.5	151.5
B	Alum + $FeSO_4$	75.0	155.0	151.0
C	Brine-acid	83.5	147.5	112.5
D	Brine-acid + $FeSO_4$	61.0	147.5	107.5
E	$CaCl_2$-HOAc	79.4	144.5	138.5
F	$CaCl_2$-HOAc + $FeSO_4$	81.2	143.0	125.5
G	NaCl-HOAc	89.5	146.0	117.0
H	NaCl-HOAc + $FeSO_4$	78.3	150.0	121.5

Mill Breakdown

The results of breakdown, on a cold mill, of some of the polymer prepared are shown in Table IV.

It is observed that although German Buna S-3 has a faster rate of mill breakdown than the Pilot Plant polymers, the deviations are not nearly as marked as they were in the heat softening data. Polymer T-213-4 during the interval 10 to 40 min. showed a greater rate of mill breakdown.

The fact that this polymer was the only one coagulated with sodium chloride–sulphuric acid may be of some significance in view of the heat softening data of Table III from which it is seen that the polymers coagulated with sodium

TABLE IV

MILL BREAKDOWN DATA

Time, min.	Mooney $ML/4'$					% Gel	
	T-213-4	T-443-80	T-525-1	1-559-1	German	T-213-4	German
0	171	158	—	131 5	161	40 9	17 4
2	174	157	—	—	160	41 5	5 4
5	173	156	112	114 0	147	39 4	0
10	170	142	106 5	93 5	127	0	0
15	146	131	99 0	83 0	102	0	0
20	120	113	84 5	76 5	93	0	0
25	—	—	—	72 5	—	—	—
30	93 5	94	—	68 5	80	0	0
40	81 5	—	59 0	60 0	72	0	0
45	—	83	—	—	—	—	—
60	—	74	—	—	—	—	—

chloride–sulphuric acid solutions showed the greatest Mooney decrease during heat softening.

Physical Test Data

Although this investigation is by no means complete, Table V illustrates some of the results obtained in examining the compounded and vulcanized sample. The polymers were compounded in the standard Rubber Reserve formula and cured at 292° F. for the times indicated.

TABLE V

PHYSICAL TEST DATA

Polymer	Mill break down	Cure min	Maximum tensile psi	Elong %	Modulus psi	Cure min	Rebound %	Cure min	Flex, in /Kc
T-199 4	30	80	4280	650	1210	85	61 4	70	15 3 × 10⁻³
T-213-4	30	90	4363	565	1708	—	—	—	—
T-443-80	15	80	4086	665	1189	—	—	—	—
T-443-80	30	85	4044	675	1175	95	59 2	80	11 3 × 10⁻³
T-443 80	60	85	4071	722	1071	95	58 6	80	10 3 × 10⁻³
T-443 80	90	90	3864	688	1142	—	—	—	—
German Buna S-3	40	50	4042	650	1220	—	—	—	—

Examination of the physical test data shows that faster rates of cure were obtained for the I. G. Farbenindustrie Buna S-3 samples. On an average, compounded in the standard recipe the German samples required a 50 min. cure at 292° F. for maximal tensile strength while the polymers prepared in the Pilot Plant averaged 85 min. for curing to maximal tensile strength.

Physical test data on compounded stock show very similar results, indicating, at least in this respect, that the quality of the European polymers is being approached.

Discussion

Failure to duplicate the Buna S-3 exactly in larger scale production in the Polymer Pilot Plant cannot be explained precisely. Perhaps more exact duplication of the German polymerization system, particularly the constant viscosity versus conversion relation, may solve the difficulty. A lower gel content and higher swelling index of the gel may result and alter the breakdown characteristics of the polymer. The effects of coagulation and drying on the properties of the polymer have not been investigated fully, but there is evidence that the coagulation step may alter the polymer considerably, and impurities left in the polymer from the polymerization, coagulation, or washing stage may affect the breakdown characteristics of the polymer. Most important, however, is the difference in agitation. The Germans used slow speed agitation, whereas the equipment used in the present investigation was high speed. This can alter the disappearance of regulators considerably and may make the molecular weight distribution entirely different. The high rate of diproxid disappearance normally (5) would suggest that it should not be sensitive to agitation.

In spite of this difference the properties of the polymers approached those of low temperature polymers (21) and surpassed those of GR-S (12, 13). However, the polymers would not be suitable for the usual factory procedure without heat softening to lower Mooney viscosities before compounding.

With the development of easily processed polymers of comparable quality the commercial application of this polymer must await development of either a suitable heat softening technique or suitable alteration in formula to enable easy processing.

Acknowledgments

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THE DIFFUSION OF LIGHT BY GROUND GLASS, WITH SPECIAL REFERENCE TO COLOR CHANGES[1]

By W. E. Knowles Middleton[2] and F. D. Smith[3]

Abstract

By special methods of grinding it has been found possible to make reproducible ground-glass surfaces. A series of six surfaces of increasing roughness was produced in crown glass, and a similar series in flint. These were illuminated at normal incidence by 2850° K. light in a photoelectric goniophotometer and intensity was measured at various angles. The apparent color temperature of the light diffused at each angle was also measured photoelectrically, with visual checks at some angles. Photomicrographs were taken of some of the surfaces, and finally the recording spectrophotometer was used to measure the diffuse reflectance, diffuse transmittance, and transmittance over a half-angle of about 8°, of several glasses. Some sandblasted samples were also studied. The transmitted light is most reddish at 0°, while at angles of more than 60° most of the glasses raise the apparent color temperature of the light. With the most finely ground glasses the color temperature at 0° reaches 2300° K. Some theoretical studies lead to the belief that most of the color changes are due to scattering, while diffraction plays a minor part.

Introduction

In comparison with other systems which diffuse light, whether translucent like opal glass or opaque like magnesium oxide, ground glass has received relatively little attention, either experimental or theoretical. A fairly extensive search of the literature since 1920 discloses only a few papers with quantitative significance. Reference may be made to articles by Schulz (10), Leontowitsch (6), Lax and Pirani (5), Kuhl (4), English (2), and Cohu (1). None of these contain any data on the change of color of the light, except in a very indirect way, exemplified by the curves for two wave lengths in the article by Kuhl (4).

There are probably two reasons for this neglect. In the first place, the surface of ground glass is very complex geometrically, and this renders the formulation of a rigorous theory extremely difficult if not impossible. Secondly, from the experimental standpoint, the difficulty of reproducing ground surfaces has probably discouraged elaborate measurements.

The present contribution does not pretend to provide a full theory of the diffusion of light by ground glass, though it will be shown later that diffraction alone is entirely inadequate to explain the observed phenomena. The second of the above-mentioned difficulties has, however, been surmounted, and we shall describe a method of making ground-glass surfaces that can be duplicated even after many months with satisfactory precision. The main emphasis in our work has been on the color changes, but data on the angular variation of

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[2] *Physicist.*

[3] *Now at the University of Rochester.*

luminance and the diffuse transmittance and reflectance will also be presented. It has been found that the changes in the color of the light can be adequately specified by means of the concept of color temperature, provided the incident light has the spectral distribution appropriate to a perfect radiator.

Preparation of the Ground Glass Samples

In the normal process of grinding glass, the abrasive breaks down very rapidly, and the roughness of the final surface depends to a very large extent on the rate at which new abrasive is supplied and the rate at which the finer broken down abrasive is carried away. The variation in pieces of ground glass, prepared in succession by the same workman using the same tools and procedures, might be small, but the variation between samples prepared by different workmen or in different workshops with the same abrasive undoubtedly will be quite large.

The samples of ground glass used for our measurements were prepared by a method which has been found to give reproducible results. The samples were ground by hand on a flat iron lap about 20 in. in diameter. A box 6 in. square (Fig. 1) carried a flat piece of sponge rubber on its underside. This

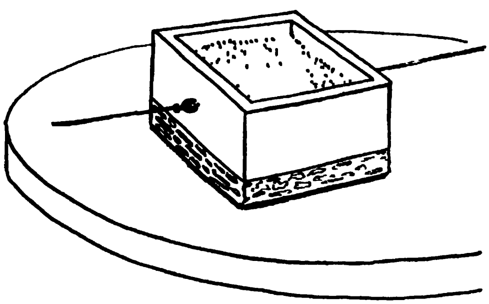


FIG. 1. *Grinding box.*

box was placed on the glass sample on the lap, and weights to give a pressure of 1 p.s.i. were added to it. Short lengths of string attached to two sides of the box were used to pull it over the surface of the lap as described below. The upper surface of the sample was protected with shellac and no serious slippage was observed.

A uniform, relatively light coating of very wet abrasive was spread on the lap and the glass drawn by means of the strings in a zig-zag fashion over the surface. A slight, rotary, to-and-fro motion with amplitude about 30° was given to the flat as it was drawn over the path. On the completion of one such "pass", as shown in Fig. 2, the lap was washed clean and the entire process repeated. The glass samples had been previously optically ground and polished, and so the time to produce a fully ground surface by the above process was reduced to a minimum. When the surface was first judged fully ground, ten extra passes were made as a safety precaution.

Samples of flint ($n_D = 1.617$) and crown ($n_D = 1.510$) glass were ground with 60, 150, and 280 mesh carborundum, 600 and 1000 mesh emery and

No. 8 garnet in decreasing order of size. The No. 8 garnet has a particle size of 8 μ. The range covered is indicated by the photomicrographs (Fig. 3) of flint samples ground with (*a*) 60 mesh carborundum, (*b*) 600 mesh emery, and (*c*) No. 8 garnet respectively. The magnification is 200 times, and the illumination by reflected light.

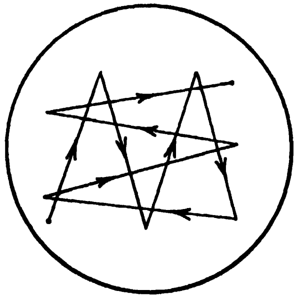


FIG. 2. *Showing motion of box in grinding.*

The General Nature of the Surfaces

As will be seen from Fig. 3, the ground surfaces appear exceedingly complex when viewed under the microscope. In every case a number of relatively large conchoidal chips have been removed, but the greater part of the surface consists of very small facets of a variety of sizes and orientations, so that the surface in this region appears to have been pounded and complex fractures can be seen. These make it appear as if scraping with some sort of sharp instrument would easily remove many of the projecting peaks of glass. The geometry of the surface appears to be the same for all the abrasives used. Thus with suitable magnification one of the surfaces ground with emery can be made to appear indistinguishable from one of the coarser carborundum-ground surfaces. The sandblasted samples were very similar to ground samples of corresponding roughness, except that the large conchoidal fractures were less numerous and relatively smaller, while the surface as a whole undulated slightly and made it difficult to bring a large area in focus at once under the microscope. This similarity in appearance between the ground and sandblasted samples may, as Preston (9) has suggested, result from the fact that the two processes are pounding processes and fundamentally the same.

Experimental Methods

Most of the measurements were made with the sample illuminated by a simple gonio-illuminator mounted on an optical bench. This apparatus, which presents no novel features, made it possible to illuminate the sample with a collimated beam at any angle of incidence, and to observe it from any angle of view in the plane of incidence, though not closer than about 20° to the direction of the beam on the incident side. The half-angle of divergence of the beam in the plane of incidence was about 1.7°. For most of the observations, a photoelectric photometer was used, fitted with filters for the measurement of color

temperature; but checks were also made by direct visual comparison in a Lummer-Brodhun photometer with a magnesium oxide screen illuminated by a sub-standard of color temperature. All the measurements were made with incident light having a color temperature of 2850° K. (I.C.I. source "A"), and nearly all at normal incidence.

In addition to the goniophotometric measurements, a recording spectrophotometer was used to measure the singly diffuse transmittance and reflectance of the samples, and also the transmission in a cone of half-angle about 8°.

Measurement of Intensity, Luminance, and Color Temperature

A photocell (R.C.A. type 926) was mounted permanently at one end of the optical bench. In front of the cell was a slit about $\frac{1}{8}$ in. wide, backed by a paper diffusing screen. This arrangement was left unaltered throughout the experiments, including calibrations.

For measurements of the angular distribution of intensity, a mask with an aperture $\frac{1}{4}$ in. wide and 1 in. high, cut in thin sheet metal, was placed in contact with the ground surface of the sample. A fixed distance from glass to cell was used. The calibration of the photocell and its associated circuits was carried out with the aid of the optical bench and a lamp run on controlled voltage. The luminance of the ground-glass surface was not measured directly, but was calculated by dividing the intensity by the cosine of the angle of view.

The measurement of color temperature was carried out by measuring the relative response of the photocell when two filters, one red and the other blue, were separately placed in front of it. A color temperature sub-standard lamp and a magnesium oxide screen were used for calibration. In order to define the illuminated area, a mask with a $1\frac{1}{2}$ in. diameter opening was placed in contact with the sample. By varying the distance from sample to photocell, and by the use of an auxiliary adjustable slit, it was easy to perform all the measurements, including calibration, at about the same level of photocell output. The angle of view was in all cases less than the angular divergence of the incident beam.

It has been pointed out by various authors (7, 12) that this way of measuring color temperature tacitly assumes that the spectral distribution of the light is similar to that of a black body. For this reason it was felt to be necessary to make some visual comparisons between the color of the light from the ground glass and of that from a magnesium oxide screen illuminated by a color temperature sub-standard; this was done by modifying a Lummer-Brodhun photometer by the addition of inclined mirrors (11, p. 209). As will be shown below, the results of these measurements (and of spectrophotometric determinations) support the validity of the photoelectric method.

Results

Angular Distribution of Luminance

It is felt to be more useful to state the angular distribution of luminance than of intensity, because this facilitates comparison with a perfect diffuser,

PLATE I

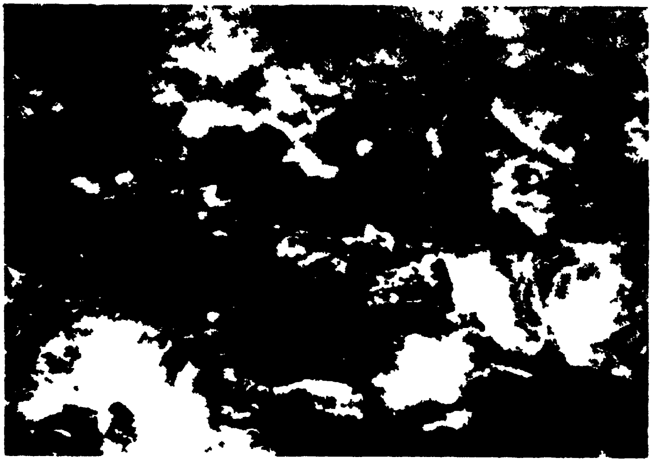


FIG. 3 (*a*)

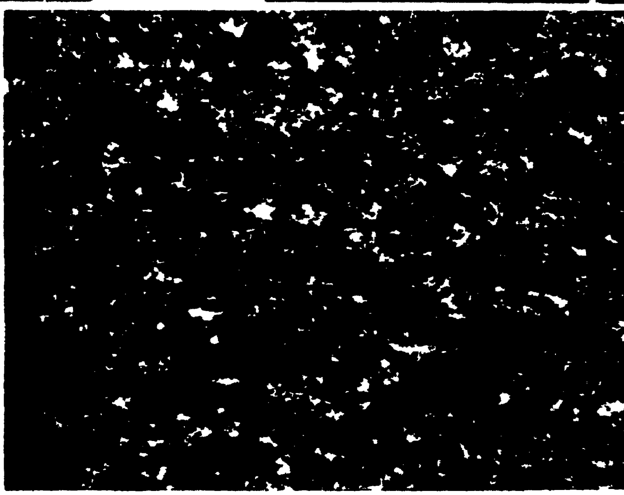


FIG. 3 (*b*)

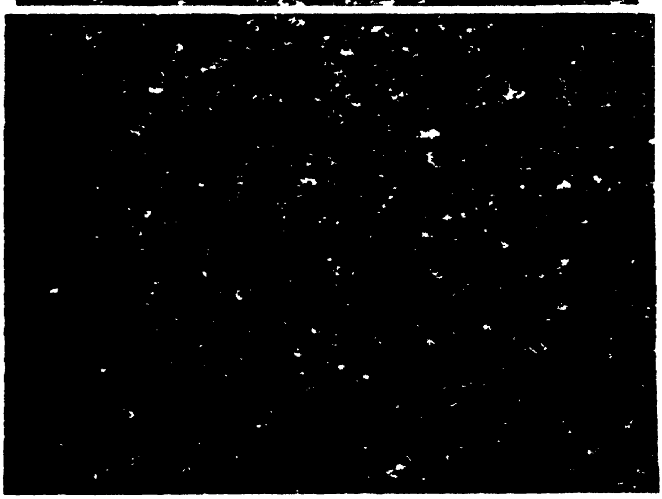


FIG. 3 (*c*)

FIG. 3. *Photomicrographs of ground surfaces (×200) by reflected light.*

the luminance of which is the same at all angles. The curve for the perfect diffuser would appear as a horizontal straight line in this method of plotting.

In Fig. 4 we present data for three different grinds of crown glass, including the coarsest and the finest; and it will at once be seen that there is little difference in their diffusing power. All the curves in Fig. 4 refer to light incident

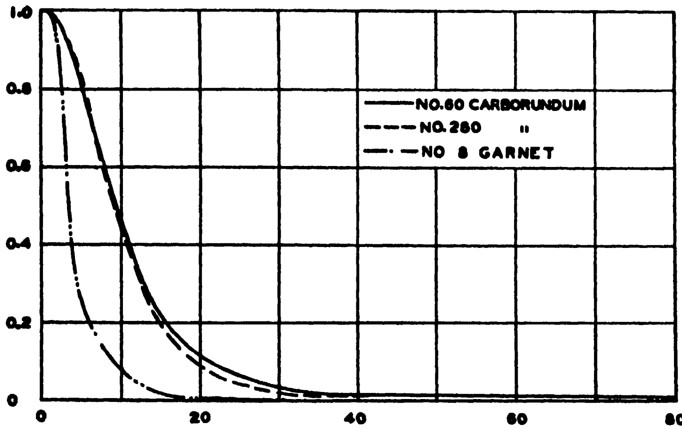


FIG. 4. *Angular distribution of luminance. Light incident normally on ground side. Crown glass, grinds No. 60, No. 280, and No. 8.*

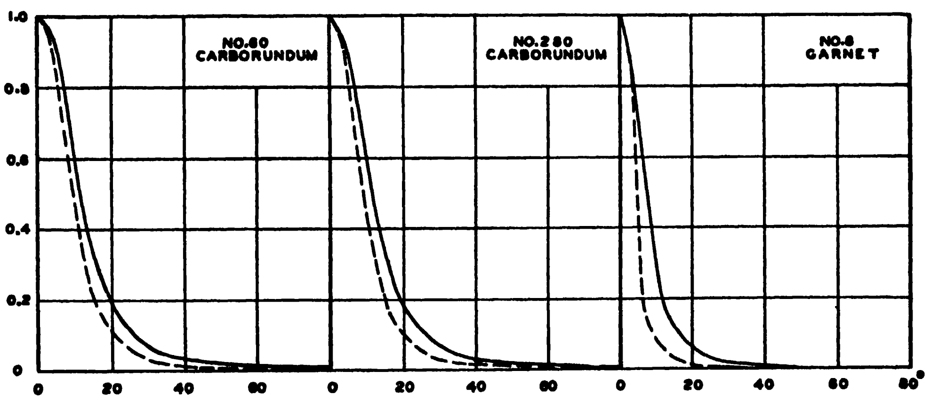


FIG. 5. *Angular distribution of luminance. Light incident normally on ground side. Solid curves—flint glass. Broken curves—crown glass.*

on the ground side, as do those of Fig. 5, which compare crown and flint glass. The flint glasses are notably better diffusers, an important practical consideration.

There is a small but interesting difference (Fig. 6) between the results for incidence on the ground side and on the polished side. The latter orientation leads to about twice the luminance at very large angles, presumably because a good deal of the back-reflected light from the ground side is incident internally on the polished side at more than the critical angle, and is totally reflected.

Even sandblasted glasses present much the same appearance (Fig. 7). This figure shows clearly the much greater importance of the type of glass than of the particular details of sandblasting technique.

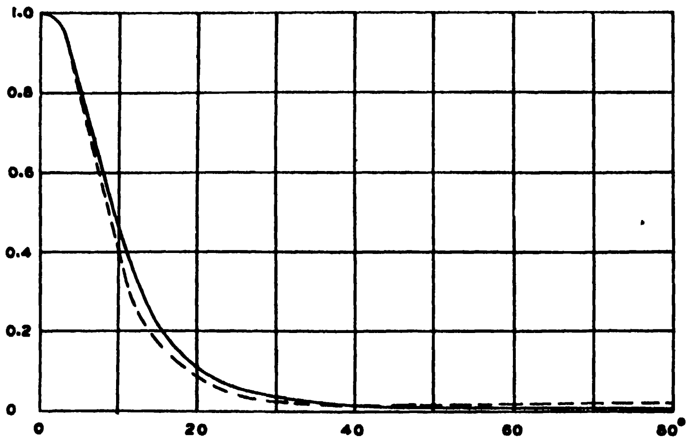


Fig. 6. *Angular distribution of luminance. Crown glass, No. 60 grind. Solid curve—light incident on ground side. Broken curve—light incident on polished side.*

All the curves, both for ground glass and for sandblasted, can be fitted quite well to a Gaussian curve of error at angles below about 15°.

Table I gives the values of the angles of view at which the brightness falls to one-half and one-tenth of the value at 0°. In every case the light is incident on the rough side.

TABLE I

Abrasive	Crown glass		Flint glass	
	θ for $B = 0\ 5B_0$	θ for $B = 0\ 1B_0$	θ for $B = 0\ 5B_0$	θ for $B = 0\ 1\ B_0$
Ground glasses				
60 mesh carborundum	9 5°	21 1°	11 4°	26 7°
150 mesh carborundum	9 6	21 9	—	—
280 mesh carborundum	9 3	19 5	11 6	25 0
600 mesh emery	8 6	17 7	9 4	22 1
1000 mesh emery	6 4	14 1	8 8	19 9
No. 8 garnet	4 4	8 5	6 4	15 9
Sandblasted glasses				
200/40	9 6	22 0	12 5	29 1
200/70	9 7	23.0	—	—
100/40	10 1	23 6	—	—
100/70	10 9	24 5	14 2	32.1

The sandblasted samples are evidently somewhat more effective diffusers, although in appearance they have the roughness of glass ground with about 150 mesh carborundum. It is also noted that all samples of a given glass ground with carborundum are very similar in their diffusion properties in spite of a wide range (about 5 to 1) in coarseness.

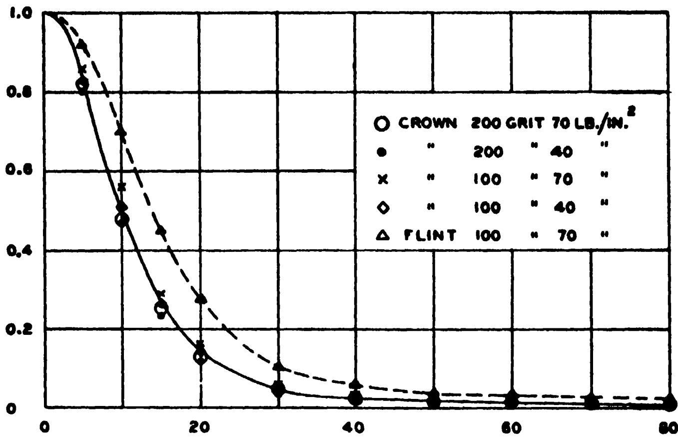


FIG. 7. *Angular distribution of luminance, sandblasted samples.*

Color Temperature Changes

Some of the results of the photoelectric color temperature measurements are shown in Figs. 8 and 9 for crown and for flint glass, illuminated by 2850° K. light incident normally. In every instance the transmitted light is reddest at small angles of view, but it will be noted that the change in color is less marked for the rougher surfaces. The great lowering of the color temperature at low

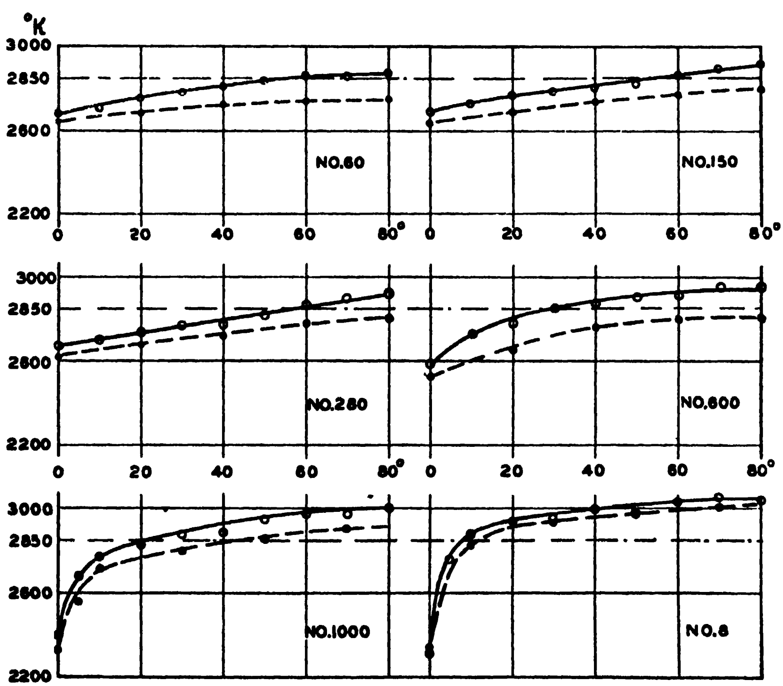


FIG. 8. *Change of color temperature with angle of view. Crown glass, 2850° K. light incident normally. Solid curves—incident on ground surface. Broken curves—incident on polished surface.*

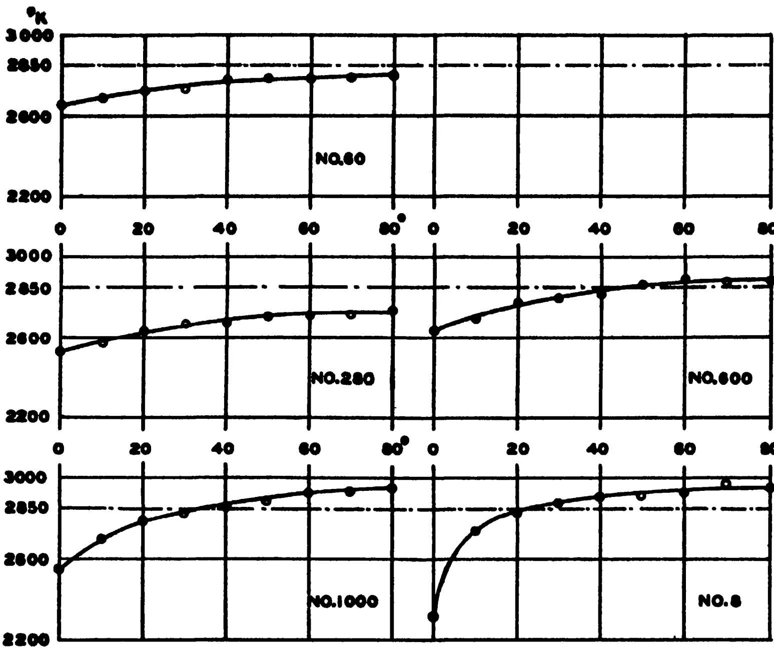


FIG. 9. *Change of color temperature with angle of view. Flint glass, 2850° K. light incident normally on ground surface.*

angles of view in the case of finer surfaces is believed due to scattering; this will be discussed below. The curves for flint glasses are lower in every case than those for the corresponding crown samples, and this may be ascribed to the loss by total reflection of light of shorter wave lengths, which would be more pronounced for the flint glass. The curves for flint glass are all for light incident on the ground surface. The angle at which the color temperature is equal to that of the incident light (2850° K.) can be read from Figs. 8 and 9. It varies fairly systematically with the coarseness of the grind. When the light is incident on the ground surface the color temperatures observed are higher, as shown by the curves for crown glass (Fig. 8).

This higher value of color temperature can be explained by reference to

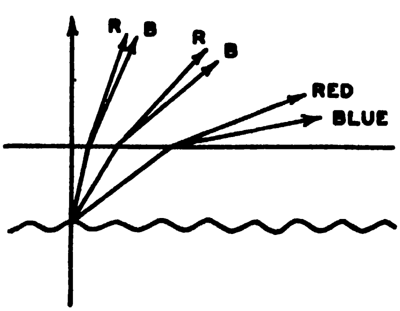


FIG. 10. *Diagram showing probable mechanism producing the difference between the two sets of curves in Fig. 8.*

Fig. 10. If we suppose that the color of light leaving the rough interface at a given angle is the same for the two cases, then for incidence on the rough surface, refraction at the second, polished, surface will cause a further spectrally selective diffusion of the light. One would expect the color to be only very slightly changed at 0° and to have a maximum change at the largest angle. The fact that the curves show an increase in the effect with angle of view supports this explanation, and total reflection will also take place at a smaller angle for the shorter wave lengths. However, some other process must operate to produce the effect near 0°.

Visual Measurements of Color Temperature

Visual measurements of color temperature were later made by the method described above (p. 154). The values (Table II) so obtained tended to be slightly lower than those obtained photoelectrically, but, except for light at small angles from finely ground surfaces, the difference was never greater than 35° K. and in most cases 20° K. or less. The larger (and positive) discrepancies (up to 45° K.) for the finely ground samples probably resulted from the circumstance that the included angle was somewhat greater (up to 4°) than that used for the other measurements. Thus it would be expected from the steepness of the curve in the region near $\theta = 0°$ that too high a value would be obtained.

TABLE II

COLOR TEMPERATURE CHANGES OBTAINED VISUALLY AND PHOTOELECTRICALLY. LIGHT (2850° K.) INCIDENT ON GROUND SIDE

Glass sample	θ, degrees	*CT* observed visually, T_V	*CT* observed photo-electrically, T_P	Difference $T_V - T_P$
No. 60 Crown	10	2670	2700	−30
	20	2745	2750	− 5
	30	2850	2780	−30
	40	2790	2800	−10
	60	2835	2855	−20
No. 280 Crown	10	2685	2700	−15
	20	2790	2720	−20
	30	2745	2765	−20
No. 600 Crown	0	2550	2580	−30
	10	2700	2710	−10
	20	2755	2790	−35
	40	2915	2890	+25
	60	2925	2935	−10
No. 8 Crown	0	2350	2305	+45
	5	2800	2760	+40
	10	2870	2880	−10
	20	— intensity too low for match.		

It is important to record here that a satisfactory match was obtainable in every instance, a fact which justifies the employment of the concept of color temperature to specify the color of the light transmitted by these glasses.

Spectrophotometric Measurements

Measurements with the recording spectrophotometer indicate that the colors of the transmitted light are very close to the Planckian locus. Some of the resulting colors, calculated from the diffuse spectral transmittances, are shown in Fig. 11, and from spectral transmittances in an 8° cone in Fig. 12. It

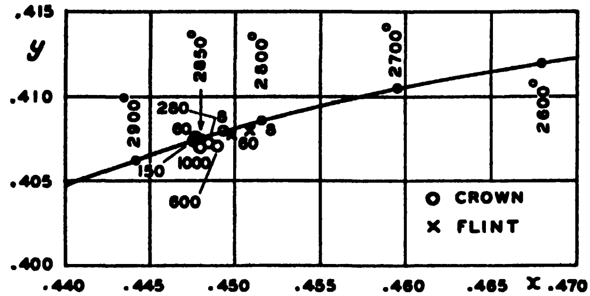


FIG. 11. *Portion of the I.C.I. chromaticity diagram, showing calculated chromaticities of diffusely transmitted light from a 2850° K. source, and also a portion of the Planckian locus. Light incident on ground side.*

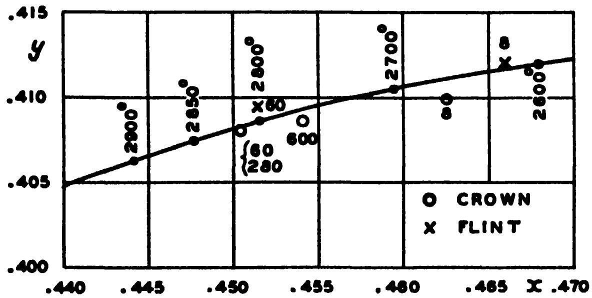


FIG. 12. *Portion of the I.C.I. chromaticity diagram, showing calculated chromaticities of light from a 2850° K. source transmitted in a cone of 8° half-angle. Light incident on ground side.*

should be noted that the spectrophotometric results are for geometrical conditions very different (regarding collection of light) from the photoelectric results. The color of the transmitted light is scarcely changed from that of the incident light if all the transmitted light is collected (Fig. 11); but the light in the 8° cone is distinctly redder, the more finely ground glasses changing the color more. It is probably not significant that the points for the four crown glass samples lie on the purple side of the Planckian locus, while the flint glass samples are on the green side, since the displacements are not much more than the experimental errors.

Diffuse 'reflectance* was also measured with the spectrophotometer and again the colors, more bluish in this case, were close to the Planckian locus.

Reproducibility of Ground Surfaces

A comparison of Figs. 8 and 9 will disclose the absence of grind No. 150 from the series of flint glass samples. Two samples of glass, supposed to be

* *The sample backed by a hollow blackened enclosure.*

crown and flint, had been ground with 150 mesh carborundum, and when they were tested in the goniophotometer they proved to be identical within the error of the experiments. A refractometer showed that they were in fact both crown glass, $n_D = 1.510$. These were, of course, prepared at about the same time in June, 1947. To determine whether samples could be reproduced after the lapse of a year, samples of No. 600 crown and No. 280 flint were prepared in the summer of 1948, and compared with the 1947 samples. The measurements of color temperature and luminance agreed almost within the errors of the experiment (Tables III and IV). Spectrophotometric measurements

TABLE III

REPRODUCIBILITY OF COLOR TEMPERATURE

θ, degrees	Color temperature, °K.		
	1948	1947	Difference, 1948 − 1947
Crown No. 600			
0	2610	2585	+25
10	2690	2705	−15
20	2760	2780	−20
30	2830	2850	−20
40	2920	2890	+30
50	2930	2920	+10
60	2945	2940	+ 5
70	2970	2930	+40
80	2965	2950	+15
Flint No. 280			
0	2620	2645	−25
10	2680	2685	− 5
20	2760	2740	+20
30	2785	2770	+15
40	2800	2780	+20
50	2800	2810	−10
60	2810	2815	− 5
70	2845	2820	+25
80	2860	2840	+20

suggest that the variation from point to point on one sample is of the same general magnitude as the difference between samples.

It should, of course, be mentioned that nearly all our samples were approximately the same size, about 3 × 3 in., though one or two were smaller. While no experiments have been made on this point, it seems likely that similar results would be obtained with samples of various sizes as long as the pressure was kept the same. It is regretted that this question was overlooked when the experiments were under way.

TABLE IV

REPRODUCIBILITY OF LUMINANCE DISTRIBUTION

θ, degrees	Relative luminance			
	Crown No. 600		Flint No. 280	
	1948	1947	1948	1947
0	1000	1000	1000	1000
5	772	767	880	872
10	389	385	570	566
15	150	151	312	315
20	67	70	166	169
30	20	19	52	55
40	8	8	23	.23
50	5	5	14	14
60	4	4	5	7
70	3	4	2	4
80	3	3	1	2

Theoretical Considerations

A theoretical explanation of diffusion by ground glass must take into account the effect of refraction, diffraction, and scattering. The experimental results however, as well as theoretical investigation, show unquestionably that refraction plays by far the largest part.

It is quite evident that an air–glass interface consisting of small facets at various angles to the normal would cause a general deviation of normally incident light, both by refraction and reflection, which would be more effective for the shorter wave lengths. Thus the light transmitted through such a surface and observed at large angles to the normal would be more bluish than the incident light. If the light is incident on the polished surface and if only a single refraction takes place for each ray, the color of light observed at 0° will be the same as that of the incident light. It is, however, quite evident that there must be multiple reflection and refraction for many of the rays passing through the surface. Some of the light observed at 0° will have undergone such a process, and since the diffusion is away from the direction of incidence and is more effective for the shorter wave lengths, we should expect therefore in any small cone of rays about the normal, an increase in the proportion of light of longer wave length. This would also mean that light reflected from the surface should be somewhat bluer than that of the source. In the case of incidence on the ground surface, we should expect that diffusion would be enhanced by the refraction effect at the second, polished, surface, causing further diffusion (Fig. 10). As previously discussed, the combination of both these effects tends to give a generally lower temperature for light transmitted at large angles, in the case where the light is incident on the polished surface. On a refraction theory, the change in color should, for a given surface geometry, be the same regardless of the degree of roughness of the surface. Furthermore, these effects should all be greater for glass of higher index of refraction.

These phenomena were all observed, and from a qualitative point of view it seems certain that most of the diffusion is due to refraction.

We may attempt a numerical evaluation of the contribution of single refractions if we consider the entire surface of the glass to be made up of a large number of prisms of all possible angles. We shall confine our discussion to incidence on the polished side of the sample. To render the problem definite, we must choose a distribution function of some sort, and it seems logical to select a probability function. Let us assume, therefore, that the projected area of surface having a slope between $\phi - \frac{1}{2}d\phi$ and $\phi + \frac{1}{2}d\phi$ is given by:

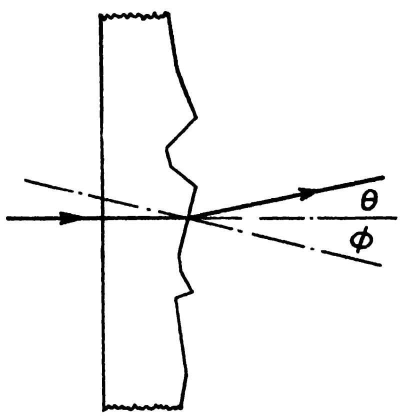
$$ds = Ae^{-h^2z^2}dz, \tag{1}$$

where

$$z = \tan\phi. \tag{2}$$

In other words, let the distribution of $\tan\phi$ follow a probability function. It may easily be shown (Fig. 13) that

$$\tan\phi = \frac{\sin\theta}{n - \cos\theta}, \tag{3}$$



$$\tan\phi = \frac{\sin\theta}{n - \cos\theta}$$

FIG. 13. *Illustrating refraction theory.*

where n is the index of refraction of the glass and θ is any angle of observation, and if we consider the flux within the conical shell defined by $d\theta$, and corresponding to $d\phi$, we obtain

$$dF = K_1 E ds = K_1 EA \frac{n\cos\theta - 1}{(n - \cos\theta)^2} \exp\left[\frac{-h^2\sin^2\theta}{(n - \cos\theta)^2}\right], \tag{4}$$

where E is the illuminance, and K_1 takes care of losses by absorption and reflection, supposed small and independent of ϕ. For the intensity we then obtain

$$I = \frac{dF}{d\omega} = KE\frac{n\cos\theta - 1}{(n - \cos\theta)^2\sin\theta} \exp\left[\frac{-h^2\sin^2\theta}{(n - \cos\theta)^2}\right], \tag{5}$$

where

$$K = \frac{K_1 A}{2\pi}$$

The choice of h must be made from the experimental results. If we take a mean value for n we may choose h to make the intensity curve fit at any point we wish. Fig. 14 shows the result of doing this at the point where the intensity has fallen to one tenth. The theory fits the experimental curve

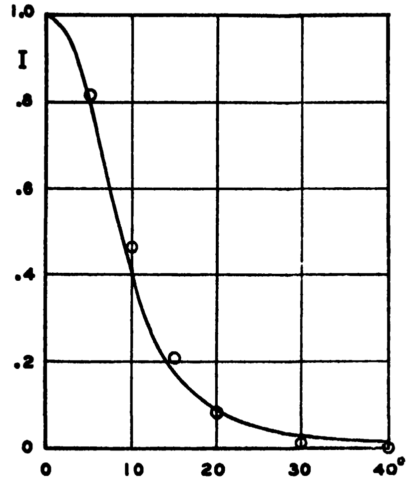


FIG. 14. *Intensity vs. angle of view. Crown glass, No. 60 grind, light incident on polished side. Circles show result of simple refraction theory; solid line denotes experimental results.*

quite well out to about 20°, but of course it cannot be expected to be satisfactory at high angles of view near the critical angle, where multiple reflections must be involved to give any light at all. This is for a coarsely ground glass. For the very fine glasses, the fit is not as good, though it is certain that refraction still plays the major role.

We do not wish to claim too much for this simple analysis. Nevertheless, in our opinion it seems probable that most of the diffusion at medium angles is produced in this way, and a probability distribution of slopes may not be far from the truth. An attempt was made to calculate the distribution of color temperature on the basis of this theory, using Hartmann's dispersion formula (3, p. 115) for n; but the amount of computation required turns out to be unjustifiably great.

It is quite obvious, at any rate, that the change of color temperature at 0° cannot be explained by a theory depending solely on refraction. The results shown in Figs 8 and 9, in which the reddening of the light at small angles is seen to depend mainly on the fineness of the grinding, make it most likely that this is a pure scattering phenomenon. A further investigation of the polarization phenomena, which should accompany this, is desirable.

The third possible mechanism of diffusion is diffraction by the small irregularities of the glass, considered as obstructing bodies.

On a diffraction theory one should expect a marked change in color with the coarseness of the grind. This was not observed with the rougher surfaces,

but was very evident with the very fine surfaces. On the other hand, little change should occur between crown and flint samples if diffraction is the main cause of the effect; but marked differences did occur, which were larger than could be attributed to the difference in roughness for a given abrasive due to the difference in hardness of the two glasses. (The flint samples are somewhat coarser than those of crown because the glass is somewhat softer, though the difference is considerably less than the steps of roughness between successive grades of abrasive). Furthermore, the diffraction does not explain the increased redness observed at low angles of scattering, for according to this theory the color at 0° should be the same as that of the source, becoming redder as the angle of view increases. Nevertheless, it was thought desirable to estimate the contribution of diffraction to the intensity at various angles.

Consider the ground surface of the glass to be made up of a very large number of circular obstructing particles, of various radii r, and in numbers distributed according to the law

$$P(r) = A^{-h^2(r-r_0)^2}. \tag{6}$$

If we direct our attention only to the particles of some one radius r, we can apply the theory of the corona (8, p. 470). Let there be P particles of radius r, and observe them from an angle θ to the direction of the incident light; then the flux per unit solid angle in the direction θ is

$$I = EP\pi^2r^4\left[1 - \frac{1}{2}\frac{m^2}{1} + \frac{1}{3}\frac{m^4}{(1.2)^2} - \frac{1}{4}\frac{m^6}{(1.2.3)^2} + \ldots\ldots\right]^2, \tag{7}$$

in which

$$m = \frac{\pi r \sin\theta}{\lambda},$$

where λ is the wave length of the light. Tables of I as a function of m are available (8, p. 479) for $P = 1$.

If we keep λ and θ constant, we may calculate I as a function of r, and then let r vary, integrating mechanically to obtain

$$I_{\lambda\theta} = \int_0^\infty F(r) \,.\, P(r)dr. \tag{8}$$

This procedure was carried out for a distribution of particles with a mean radius r_0 (Equation 6) of 2μ, and a value of h such that the number of particles of radius 20 μ is 1/100 of the number of radius 2μ. This is a very fine grind. Using a wave length of 550 mμ, the intensity at $\theta = 3°$ was found to have fallen to about 1/30 of that at $\theta = 0°$, and to less than 1/100 at $\theta = 6°$. This may be compared with any of the curves of Figs. 5 to 7. Other distributions of particle sizes cannot materially improve the result, and it must therefore be concluded that diffraction plays a minor part in the process even with the more finely ground surfaces. This conclusion was also reached by Leontowitsch (6), who endeavored to explain the phenomenon on the basis of the electromagnetic

theory of light. He found that diffraction was an adequate explanation only for very fine, almost invisible surfaces.

Summarizing our theoretical findings, we may say that refraction, scattering, and diffraction contribute in that order to the total diffusion of light by ground glass, with refraction playing by far the largest part.

Conclusion

In this paper we have presented a method of making reproducible ground-glass surfaces, and also the results of measurements of the light transmitted by ground and sandblasted glass at various angles, in particular of the color temperature of the light. An attempt has also been made to give an elementary theoretical account of the phenomenon.

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THE MECHANICAL BEHAVIOR OF GUY WIRES[1]

By J. W. Campbell[2]

Abstract

The general manner in which guy wires behave is well known, but in this paper the problem is treated by means of new catenary formulae which are especially convenient for the purpose. The behavior is discussed in detail, and there is given a simple practical means of designing a set of guy wires which will serve any preassigned purpose. The method is illustrated by numerical examples.

Introduction

When a column is supported by a set of guy wires each wire hangs in the form of a catenary. The wires each exert a lateral force on the column, and when the column is vertical these lateral forces balance one another. Then when a lateral external pressure is exerted on the column, by wind, for example, the column must sway. The sway will increase the tensions of the wires on one side and decrease the tensions on the other side. The increase will exceed the decrease and the sway of the column will increase until equilibrium is established with the external pressure.

There will also be an absorption of energy which will re-establish the column to the vertical position when the external pressure ceases.

If the wires are pulled to too high a tension in the vertical position the tensions arising from an extreme external pressure may be the maximum allowable, and if they are not taut enough the column will experience too great a sway before a sufficient restoring force is built up.

The Behavior of a Single Wire

We let the positions of the lower and upper ends be (0, 0) and (x, y). We also let T be the tension at the upper end, H the horizontal tension, s the length of the wire, and w the weight per unit length.

Then we have the relations (2, p. 248)

$$y = x \sinh k' \frac{\sinh u}{u} \tag{1}$$

$$s = x \cosh k' \frac{\sinh u}{u} \tag{2}$$

$$T = \frac{wx}{2} \frac{\cosh (k' + u)}{u} \tag{3}$$

$$H = \frac{wx}{2u} \tag{4}$$

$$y/s = \tanh k' . \tag{5}$$

[1] *Manuscript received August 19, 1948.*
Contribution from the Department of Mathematics, University of Alberta, Edmonton, Alberta.

[2] *Professor of Mathematics.*

The k' and u are parameters, and their meanings may be taken as given by Equations (4) and (5).

When the column sways, x varies but y may be taken as constant. In fact all the symbols in these equations vary except y and w, although the variations of some are more appreciable than those of others. The variations of s and k', for example, are slight.

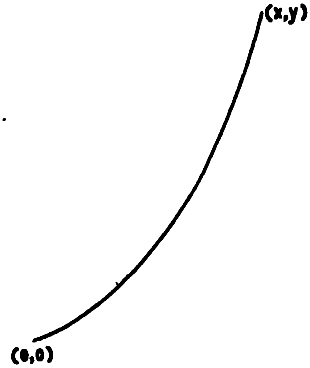

FIG. 1

We shall designate by subscripts 1 and 2 the values of these varying symbols without and with sway. Then we have the relations:

Without sway		With sway	
$y = x_1 \sinh k_1' \dfrac{\sinh u_1}{u_1}$	(6)	$y = x_2 \sinh k_2' \dfrac{\sinh u_2}{u_2}$	(11)
$s_1 = x_1 \cosh k_1' \dfrac{\sinh u_1}{u_1}$	(7)	$s_2 = x_2 \sinh k_2' \dfrac{\sinh u_2}{u_2}$	(12)
$T_1 = \dfrac{wx_1}{2} \dfrac{\cosh (k_1' + u_1)}{u_1}$	(8)	$T_2 = \dfrac{wx_2}{2} \dfrac{\cosh (k_2' + u_2)}{u_2}$	(13)
$H_1 = \tanh k_1'$	(9)	$H_2 = \tanh k_2'$	(14)
$y/s_1 = \tanh k_1'$	(10)	$y/s_2 = \tanh k_2'$	(15)

The restoring horizontal force arising from the sway and due to this wire is therefore

$$\frac{w}{2}\left(\frac{x_2}{u_2} - \frac{x_1}{u_1}\right), \tag{16}$$

and the moment of this restoring force about the base is

$$\frac{wy}{2}\left(\frac{x_2}{u_2} - \frac{x_1}{u_1}\right). \tag{17}$$

There is another relation, involving the modulus of stiffness of the wire. Denoting that modulus by λ we have

$$T = \lambda \frac{s - s_0}{s_0}, \tag{18}$$

where s_0 is the unstretched length.

Then

$$s_2 = s_1 + \frac{T_2 - T_1}{\lambda} s_0 \, ,$$

and since λ is large and $s_1 - s_0$ is small, no appreciable error will be involved if we write

$$s_2 = s_1 + \frac{T_2 - T_1}{\lambda} s_1 \, . \tag{19}$$

The Energy Absorbed in the Sway

The energy absorbed will arise from two sources, viz., the work done by the horizontal force H in varying x, and the work done by T in stretching the wire.

The first of these is

$$\int_{x_1}^{x_2} H\, dx \, .$$

Now from Equation (1)

$$x = \frac{y}{\sinh k'} \frac{u}{\sinh u} \, ,$$

whence

$$dx = \frac{y}{\sinh k'} \, d\left(\frac{u}{\sinh u}\right) ,$$

if we neglect the variation of k'.

Therefore

$$H\, dx = \frac{wx}{2u} dx = \frac{wy^2}{2 \sinh^2 k'} \frac{1}{\sinh u} d\left(\frac{u}{\sinh u}\right) ,$$

and

$$\int_{x_1}^{x_2} H\, dx = \frac{wy^2}{2 \sinh^2 k'} \left[\frac{1}{\sinh u} \frac{u}{\sinh u} - \int \frac{u}{\sinh u} d\left(\frac{1}{\sinh u}\right) \right]_{u_1}^{u_2}$$

$$= \frac{wy^2}{8 \sinh^2 k'} \left[\frac{2u - \sinh 2u}{\sinh u} \right]_{u_1}^{u_2} .$$

Since the tension varies linearly as the stretch it follows that the energy absorbed in stretching the wire is

$$\frac{1}{2} (T_1 + T_2)(s_2 - s_1) \, .$$

Therefore the total energy absorbed in the sway is

$$\frac{wy^2}{8 \sinh^2 k'} \left[\frac{2u - \sinh 2u}{\sinh u} \right]_{u_1}^{u_2} + \frac{1}{2} (T_1 + T_2)(s_2 - s_1) \, . \tag{20}$$

Method of Solution

If y, x_1, x_2, u_1, and w are given we may proceed in the following manner:

(1)′ By means of (6) find k_1'.

(2)′ For a first approximation put $k_2' = k_1'$ in (11) and find u_2.

(3)′ Find T_1 and T_2 from (8) and (13).

(4)′ Find s_1 from (7) and then find s_2 from (19).

(5)′ From the result of (4)′ and (15) find k_2', second approximation.

(6)′ Repeat (2)′ to (5)′ until no further change in k_2' occurs.

The values of the restoring force, restoring couple, and the energy absorbed may then be calculated.

This is a general solution, but in practice it admits of simplification in most cases. For the λ is usually so large that no appreciable effect is afforded by (19). A variation of T which would make the effect of (19) appreciable would put the tension beyond the breaking point. Then both s and k' will be unchanged and (1)′ and (2)′ give the solution.

There is, however, an important technique of solution.

Technique of Solution

Instead of solving (6) for k_1', we may take the ratio of (11) to (6) and obtain

$$\frac{\sinh u_2}{u_2} = \frac{\sinh u_1}{u_1} \div \frac{x_2}{x_1}$$

Now x_2/x_1 is nearly 1, and denoting it by $1 + a$ then a is small. Also, $(\sinh u)/u$ is greater than 1 but not greatly different from 1.

Then

$$\frac{\sinh u_2}{u_2} = \frac{\sinh u_1}{u_1} \div (1 + a) \; .$$

This is a convenient form for numerical work.

For example, suppose that a column were guyed by cables running from the ground at 50 ft. from the foot of the column to a point 70 ft. high on the column. Suppose the cable were installed so that when the column was vertical the parameter $u = u_1$ was 0.2025 and that the cables weighed 1.55 lb. per ft. Consider the effect on two opposing cables of a sway which would move the point of attachment by 0.006×50 ft. in their plane.

For each cable we should have, with forces in lb._w and lengths in ft.,

$$\frac{\sinh u_1}{u_1} = 1.00685, \quad H_1 = \frac{wx_1}{2u_1} = \frac{1.55 \times 50}{2 \times 0.2025} = 191 \; .$$

For the one with span increased we should have

$$\frac{\sinh u_2}{u_2} = 1.00685 \div 1.00600 = 1.00085,$$

$$u_2 = 0.0715,$$

$$H_2 = \frac{wx_2}{2u_2} = \frac{1.55 \times 50 \times 1.006}{2 \times 0.0715} = 545 \; .$$

For the one with span decreased we should have

$$\frac{\sinh u_2}{u_2} = 1.00685 \div 0.994 = 1.00685 \times 1.00604 = 1.01291,$$

$$u_2 = 0.2778,$$

$$H_2 = \frac{1.55 \times 50 \times 0.994}{2 \times 0.2778} = 138.$$

The restoring force on the column by these two cables would therefore be $545 - 138 = 407$ lb.$_w$, and its moment about the base would be 407 lb.$_w$ $\times$ 70 ft. = 28,490 ft. lb.$_w$.

For each one*

$$\sinh k' = \frac{70}{50} \div 1.00685 = 1.392,$$

$$k' = 1.133.$$

Therefore the tension of the one with increased span is

$$545 \cosh (1.133 + 0.072) = 545 \times 1.818 = 990 \text{ lb.}_w$$

Method of Application to Practical Problems

This illustration suggests a practical means of adjusting a set of cables when they are set up, in order to serve a designed purpose.

Suppose, for example, that the y, x_1, and w have been chosen, and that it is desired to adjust the cables (find the value of u_1) so that a pair of opposing cables will, in extreme conditions, afford a restoring moment N about the base without the tension of either cable exceeding a limit P.

We proceed as follows:

Take u_2 and u_3 as the parameters of the opposing cables at extreme sway. Find u_2 with $x_2 = x_1$ and $T = P$, since the variation in x is small.

From the tables (1, Table XVII) read

$$\frac{\sinh u_2}{u_2} = 1 + b_2 . \tag{21}$$

Then

$$\frac{wx_3}{2u_3} = \frac{wx_2}{2u_2} - \frac{N}{y}, \quad u_3 = \frac{wx_1}{2} \div \left(\frac{wx_1}{2u_2} - \frac{N}{y}\right). \tag{22}$$

From the tables read

$$\frac{\sinh u_3}{u_3} = 1 + b_3 . \tag{23}$$

Then

$$1 + a = 1 + \frac{b_3 - b_2}{2}, \tag{24}$$

and

$$\frac{\sinh u_1}{u_1} = 1 + \frac{b_2 + b_3}{2}. \tag{25}$$

* *Seeing that k' does not change in value in our solution we may for convenience drop the subscript.*

Alternatively, the maximum tension P might have been specified and the maximum sway c at the height y.

Then u_2 is determined with $x_2 = x_1$ and $T = P$, and b_2 is given by(21). Also,

$$a = c/x_1 \; . \tag{26}$$

Therefore

$$\frac{\sinh u_1}{u_1} = 1 + b_2 + c/x_1 \; , \tag{27}$$

whence u_1 is determined.

Likewise

$$\frac{\sinh u_3}{u_3} = 1 + b_2 + 2c/x_1 \; , \tag{28}$$

whence u_3 is determined.

Then the resisting moment about the base is

$$\frac{wx_1y}{2}\left(\frac{1}{u_2} - \frac{1}{u_3}\right) . \tag{29}$$

If this resisting moment is not sufficiently great it can be increased by increasing some or all of w, x_1, and y.

Application

Problem

It is proposed to support a column by a set of four guy wires anchored to the ground 60 ft. from the base and attached to the column 80 ft. from the ground. What should be the setting parameter of the cables if a tension of 1800 lb._w is not to be exceeded and an extreme resisting moment about the base of 60,000 ft. lb._w is to be provided, assuming the cables to weigh 1.85 lb. per ft.? What will be the extreme sway at the 80 ft. level (1) if the extreme external pressure is experienced in the plane of two of the wires, and (2) if the direction of external pressure bisects the angle between the two planes of wires?

Solution

With forces in lb._w and lengths in ft., we are given

$$x_2 = x_1 = 60, \quad y = 80, \quad P = 1800, \quad N = 60{,}000, \quad w = 1.85.$$

From (1) and (3),

$$\sinh k_2' = \frac{y}{x_2} \div \frac{\sinh u_2}{u_2}, \quad u_2 = \frac{wx_2}{2P} \cosh (k_2' + u_2) \; ,$$

and we solve by successive substitution.

$$\frac{y}{x_2} = 1.3333, \quad \frac{wx_2}{2P} = \frac{1.85 \times 60}{2 \times 1800} = 0.0308.$$

Approx.	u_2	$(\sinh u_2)/u_2$	$\sinh k_3'$	k_3'	$k_3' + u_2$	$\cosh (k_3' + u_2)$	u_2
1	0	1.00000	1.3333	1.0984	1.0984	1.6664	0.0513
2 ·	0.0513	1.00044	1.3328	1.0983	1.1496	1.7368	0.0535
3	0.0535	1.00048	1.3327	1.0982	1.1517	1.7399	0.0536
4	0.0536	1.00048	1.3327	1.0982	1.1518	1.7400	0.0536

$$\therefore\ u_2 = 0.0536\,.$$

Then, by (4),

$$H_2 = \frac{wx_2}{2u_2} = \frac{1.85 \times 60}{2 \times 0.0536} = 1034\,.$$

Resisting force at extreme $= 60{,}000/80$ lb.$_w$ $= 750$ lb.$_w$.

$$\therefore\ H_3 = 1034 - 750 = 284\,,$$

$$u_3 = \frac{1.85 \times 60}{2 \times 284} = 0.1953\,.$$

Then

$$\frac{\sinh u_2}{u_2} = 1.00048, \quad \frac{\sinh u_3}{u_3} = 1.00637\,,$$

$$\frac{\sinh u_1}{u_1} = 1 + \frac{0.00048 + 0.00637}{2} = 1.00343\,,$$

$$u_1 = 0.1434\,,$$

$$a = 0.00343 - 0.00048 = 0.00295\,,$$

$$80a = 0.236\,.$$

Hence the sway at the 80 ft. level for extreme pressure is 0.236 ft. or 2.83 in.

To answer the second question, with the direction of external pressure bisecting the angle between the two planes of the cables each opposite pair of the cables would provide half the resisting force, that is, 375 lb.$_w$. Also, if the sway of the column were $80a$, then the sway in the planes of the cables would be $80a \cos 45°$.

Now if the parameters of an opposing pair of cables at extreme sway were u_2 and u_3, then

$$\frac{1.85 \times 60}{2}\left(\frac{1}{u_2} - \frac{1}{u_3}\right) = 375\,,$$

or

$$\frac{1}{u_2} - \frac{1}{u_3} = 6.76\,.$$

One solves this equation by bracketing:

$$u_1 = 0\ 1434, \quad (\sinh u_1)/u_1 = 1\ 00343$$

$$(\sinh u_2)/u_2 = (\sinh u_1)/u_1 - a \cos 45°, \quad (\sinh u_3)/u_3 = (\sinh u_1)/u_1 + a \cos 45°.$$

$a \cos 45°$	$(\sinh u_2)/u_2$	$(\sinh u_3)/u_3$	u_2	u_3	$1/u_2$	$1/u_3$	$\frac{1}{u_2} - \frac{1}{u_3} - 6\ 76$
0 002	1 00143	1 00543	0 0927	0 1805	10 79	5 54	− 1 51 $\frac{15}{93} = 0.2$
0 003	1 00043	1 00643	0 0510	0 1963	19 61	5 09	+ 7 76
0 0022	1 00123	1 00563	0 0860	0 1837	11 63	5 46	− 0 59
0 0023	1 00113	1 00573	0 0823	0 1853	12 15	5 40	− 0 01
0 0024	1 00103	1 00583	0 0787	0 1868	12 71	5 37	+ 0 58

$$\therefore a \cos 45° = 0\ 00230 .$$

Therefore the sway at the 80 ft level is

$$80 \times 0\ 00230 \times 1\ 414 = 0\ 260 \text{ ft} = 3\ 12 \text{ in}$$

One might offhand think that the sway would be greater in the plane of two cables than in the direction which bisects the angle between the two planes, since all four cables are brought into play. The reason why the sway is greater in the second case than possibly anticipated is that the resistance is not a linear function of the sway, but builds up rapidly as the sway increases.

Further Principles of Application

1. Since

$$\sinh k' = \frac{y}{x_1} \div \frac{\sinh u_1}{u_1},$$

and $(\sinh u_1)/u_1$ does not differ greatly from 1, then $wy^2/(8 \sinh^2 k')$ is very nearly $wx_1^2/8$. Also, it has already been pointed out that when λ is large the second term of (20) is negligible. Therefore the absorption of energy is, to a close approximation,

$$\frac{wx_1^2}{8}\left[\frac{2u - \sinh 2u}{\sinh u}\right]_{u_1}^{u_2}.$$

Applied to the problem just solved the absorption of energy is, in the first case 44 ft. lb.$_w$, and in the second case 52 ft. lb $_w$

2. To find the sag of a cable below the chord joining its points of support it is better to use a different form of the equations (2, p. 247), viz.,

$$\left.\begin{aligned} y &= c\left\{\cosh\left(\frac{x}{c} + k\right) - \cosh k\right\}, \\ \frac{dy}{dx} &= \sinh\left(\frac{x}{c} + k\right), \end{aligned}\right\} \qquad (30)$$

for the c and k are the same for all segments of a given catenary, whereas the u and k' depend on the segment being considered.

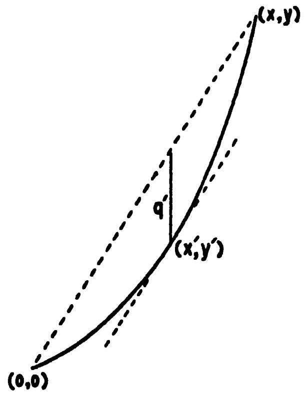

FIG. 2

The slope of the chord is y/x_1, and if (x', y') is the point where the tangent is parallel to the chord then

$$\sinh\,(x'/c + k) = y/x_1\,, \tag{31}$$

and

$$q' = \frac{x'y}{x_1} - c\left\{\cosh\left(\frac{x'}{c} + k\right) - \cosh k\right\}. \tag{32}$$

We also have

$$\frac{x_1}{2c} = u_1, \quad \frac{x_1}{2c} + k = k'. \tag{33}$$

To find q' at the initial setting we then proceed as follows:

We are given x_1, y, and u_1.
From (6) find k'.
From (33) find c and k.
Then find x' from (31).
Substitute in (32) and obtain q'.

Proceeding thus in the problem just solved we have, for each cable at time of setting, the following results:

We start with $x_1 = 60$, $y = 80$, $u_1 = 0.1434$.

We then find in succession $k' = 1.096$, $c = 209$, $k = 0.953$, $x'/c + k = 1.0986$, $x' = 30.6$, $q' = 3.7$.

The sag of the cable below the chord is therefore 3.7 ft.

Summary

In any system of guy wires the behavior of the system depends on (1) the horizontal and vertical distances of the cable attachments from the foot of the column being supported, (2) the weight of the cable per unit length, and (3) the tension to which the cables are strung.

The conditions which have to be met are (1) a maximum allowable tension under extreme sway, (2) a maximum sway for a given lateral pressure on the column, and (3) a sufficient restoring moment when a given tension or sway has been experienced.

The methods here given enable one to design a system which will serve any specified purpose, or to determine the effectiveness of a given system when it is subject to a hypothetical strain.

References

1. CAMPBELL, J. W. Numerical tables. Douglas Printing Co., Edmonton. 1946.
2. CAMPBELL, J. W. An introduction to mechanics. Pitman Publishing Corporation, New York. 1947.

NOTES

Further Remarks on "Photometry and Colorimetry of Railroad Fusees"*

In a recent paper in this journal (1), the writer described a method for the colorimetry of railroad fusees with a trichromatic colorimeter, in which it was stated that the color of the fusees was always more saturated than the colors produced by mixing the light passing through Wratten filters No. 70 (Red) and No. 74 (Green). This result was later found to disagree with the results of a different method, and a search has been made for the cause of the discrepancy.

It has now been found that, at least for some observers, a match set up for a steady light of about the same chromaticity as a red fusee is entirely unsatisfactory if the light is then made to flicker at the rate of a few times per second (i.e., well below the critical frequency). The amount of blue in the mixture required for a match is then much less. The matter is receiving further study, but I wish now to point out that the numerical results represented by Fig. 8 of the paper are inexact. The other conclusions are not affected.

1. MIDDLETON, W. E. K. Can. J. Research, F, 26 : 331-339. 1948.

* *Issued as N.R.C. No. 1894.*

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W. E. KNOWLES MIDDLETON

DIVISION OF PHYSICS,
NATIONAL RESEARCH LABORATORIES,
OTTAWA, CANADA.

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THE ADSORPTION OF SOAP BY CARBON BLACK[1]

By A. S. Weatherburn,[2] G. R. F. Rose,[2] and C. H. Bayley[2]

Abstract

The adsorption of the sodium soaps of lauric, myristic, palmitic, stearic, and oleic acids from aqueous solutions by a carbon black has been measured. The adsorption appears to be a combination of two more or less independent processes: (*a*) adsorption of neutral soap, and (*b*) adsorption of fatty acid resulting from hydrolysis. The adsorption of both the fatty acid and alkali components of the soaps studied is in agreement with the Freundlich adsorption equation over the concentration range investigated, the extent of adsorption increasing with increasing chain length of the saturated soaps examined. In every case there is a greater adsorption of fatty acid than of alkali, but this difference becomes greater with increasing chain length of the soap. Increase in temperature causes a slight decrease in adsorption, but the effect is small. On the basis of its adsorptive behavior, sodium oleate appears to have an effective chain length of about 15 carbon atoms. Excess of fatty acid in the initial soap solution results in an increased adsorption of total fatty acid, but does not influence the adsorption of neutral soap; on the other hand, excess of alkali in the initial solution not only results in an increased adsorption of total alkali, but also leads to a decrease in the adsorption of fatty acid and neutral soap. This decrease in adsorption is attributed to suppression of hydrolysis, but even with 100% excess alkali where hydrolysis must be almost completely suppressed there is still an appreciable adsorption of fatty acid which must be adsorbed in the form of neutral soap. The adsorbed material corresponds to an acid soap of variable composition, the ratio of excess acid to neutral soap depending on the composition of the initial solution, the temperature, and the particular soap used. The adsorption of soap from 95% alcohol solution and from absolute alcohol solution is essentially the same, both being considerably lower than the adsorption of the same soap from aqueous solution. In spite of the fact that hydrolysis of soap does not occur in alcoholic solution the fatty acid and alkaline components are not adsorbed in equivalent amounts, and it is suggested that, in this case, splitting of the soap is brought about by alcoholysis, followed by preferential adsorption of one of the reaction products.

Introduction

During the course of studies in the field of detergency currently in progress in these laboratories it became of interest to investigate the adsorption of various sodium soaps on carbonaceous materials used as fiber-soiling media. The present paper gives data relating to the adsorption of soaps, or their components, on one carbon which may be regarded as typical of the carbons employed in detergency studies. While these data would not be expected to apply directly to other carbons or complex carbon–oil soils which have been used by other investigators, it is believed that the work is of interest in

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[2] *Chemist.*

so far as it illustrates the general behavior of soap solutions in contact with finely divided carbonaceous material.

A survey of the literature reveals that only a limited amount of work of a quantitative nature has been reported on the adsorption of soaps by carbon.

Fromageot and Wurmser (2) measured the adsorption of a number of organic acids and their sodium salts in aqueous solution on charcoal and found that the adsorption of the acid was appreciable and was always greater than the adsorption of the salt. The difference between adsorption of acid and of salt varied widely with the various organic radicals, thus the sodium salts of formic, acetic, succinic, and citric acids were not adsorbed at all, whereas the adsorption of sodium pyruvate amounted to more than 80% of that of the free acid. They were unable to find any relation between the dissociation constant of the acid and the adsorption of the salt.

From measurements of the adsorption of various inorganic acids, salts, and bases in aqueous solution on purified low ash charcoals of both animal and vegetable origin, Miller (8) concluded that acids are adsorbed to a considerable extent, bases are not adsorbed at all, and neutral salts are not adsorbed as such, although acid resulting from their hydrolysis is adsorbed.

Mikumo (6) measured the adsorption of potassium oleate in aqueous solution on a variety of adsorbents and concluded that carbon (Merck's animal charcoal) adsorbs a complex soap, which always contains an excess of fatty acid, even from initially alkaline solutions. He points out that the presence of carbon may thus greatly promote the hydrolysis of soap owing to displacement of the hydrolysis equilibrium.

Mikumo (7) also measured the adsorption of a series of saturated potassium soaps in absolute alcohol solution on charcoal (Merck's animal charcoal purified with alcohol and ether), and found that the adsorption was in agreement with the Freundlich equation (1) up to the "concentration of aggregate-formation", the extent of adsorption increasing with increasing molecular weight of the soap.

Neville and Harris (9) measured the pH of an aqueous solution of an olive oil soap after agitation with lampblack and filtering, and found that the filtrate was more alkaline than the original solution. They attributed this increased alkalinity to the selective adsorption of either free fatty acid or acid soap by the lampblack.

Experimental

Materials and Methods

The adsorbent used throughout these experiments was uncompressed standard Micronex,* a channel black having a mean particle diameter of about 28mμ.

* *Supplied by Binney and Smith Co., New York.*

Sodium soaps of lauric, myristic, palmitic, stearic, and oleic acids were prepared from Kahlbaum or Schuchardt fatty acids following the method described by Powney (10). The melting point, acid number, and "percent purity" calculated from the acid number of the fatty acids are listed in Table I. The alcohol used in the preparation of the soaps was freed from aldehydes by refluxing with powdered zinc and potassium hydroxide, followed by distillation.

TABLE I

CHARACTERISTICS OF FATTY ACIDS USED IN PREPARATION OF SOAPS

Acid	Melting point, °C	Acid No. Mgm. KOH/gm. acid	Purity, %
Lauric	44.0	281.5	100.5
Myristic	53.0	244.0	99.3
Palmitic	62.5	216.5	98.8
Stearic	69.0	196.5	99.4
Oleic		193.5	97.4

Distilled water was used in the preparation of all aqueous solutions.

The adsorption of the fatty acid and alkali components of the various soaps was determined by the following method except where otherwise noted.

A 1.000 gm. portion of carbon black was weighed into a previously warmed 400 ml. vacuum bottle, and agitated for 10 min. with 250 ml. of soap solution having the desired temperature and initial concentration, using a mechanical shaking device. After shaking, the suspension was weighed, and filtered under suction through three thicknesses of Whatman No. 42 filter paper supported in a covered, electrically heated Buchner funnel. The filter cake and filtrate were each weighed, and any loss in weight (due to evaporation of water during filtration) was made up by the addition of distilled water to the filtrate.

A 100 ml. aliquot of the filtrate was taken for analysis and a blank determination was also carried out on 100 ml. of the original soap solution filtered in the same way. The soap solution was acidified with an excess of $N/100$ sulphuric acid, heated almost to boiling, and cooled. The liberated fatty acid was extracted with three successive portions of diethyl ether which had been previously rendered neutral by distillation over sodium hydroxide. The combined ether extracts were washed once with water, the washings being added to the aqueous residue from the extractions. The aqueous portion was boiled gently to expel dissolved ether and titrated with $N/100$ sodium hydroxide and phenolphthalein. The ether was removed from the extracted fatty acid by distillation, followed by warming on a boiling water bath. The residue was then redissolved in neutral 95% ethyl alcohol and titrated hot with $N/100$ sodium hydroxide and phenolphthalein.

The adsorption of either fatty acid or alkali is given by the formula $x = 0.25 (C_0 - C)$, where x is the quantity adsorbed in milliequivalents per gram of carbon, and C_0 and C are the concentrations of the reference and equilibrium solutions respectively in milliequivalents per liter ($M \times 10^{-3}$).

Where percentage concentrations of fatty acid or alkali are used, these are expressed in terms of the equivalent weight of sodium soap.

Preliminary Experiments

A series of preliminary experiments was carried out to determine the extent of experimental error and hence to evaluate the probable accuracy of the method.

Carbon.—A 0.4% suspension of carbon in distilled water at 70°C. was shaken for 10 min. and then filtered. No titratable amount of acid or of alkali was found in the filtrate. A similar test was carried out using 95% ethyl alcohol at 25°C. in place of the water. Again no measurable amount of acid or alkali was extracted from the carbon.

Tin foil.—It was observed that the pure tin foil used to cover the stoppers of the vacuum bottles became dull after continued use, particularly with solutions containing excess alkali. In order to determine the effect on the adsorption values of any possible reaction with the tin, pieces of foil having an area equal to 6 to 8 times that normally in contact with the solution were shaken with 250 ml. of 0.07% sodium hydroxide solution at 70°C. for 30 min. There was no detectable change in the concentration of the sodium hydroxide solution at the end of this time.

Adsorption on filter paper. Errors due to adsorption of soap by the filter paper during the filtration operation were investigated. It was found that the decrease in concentration of a 0.1% solution of sodium stearate after filtering was less than 1%. This is considered negligible and, in any case, is compensated for by filtration of the reference solution prior to analysis.

Rate of adsorption.— The adsorption of fatty acid and alkali from a 0.1% solution of sodium stearate was determined for a range of shaking times varying from 5 to 80 min. It was found that equilibrium was established within the first five minutes and that no further adsorption took place on longer shaking. Nevertheless, in order to allow an adequate margin of safety, a shaking time of 10 min. was adopted for all subsequent work.

Over-all errors.—Errors arising from all sources, which may include mechanical losses in handling, inaccuracy in measurement, effect of atmospheric carbon dioxide, and adsorption by glass and filter paper, were evaluated by working through the complete procedure using a 0.1% solution of sodium stearate, but omitting the carbon. The apparent adsorption obtained was 0.017 and 0.021 milliequivalents per gm. for fatty acid and alkali respectively. This represents an error in the adsorption data for 0.1% sodium stearate of 2.4 to 4.3%.

Effect of Soap Concentration on Adsorption

The adsorption of fatty acid and of alkali from aqueous solutions of sodium laurate and sodium stearate of initial concentration varying from 0.01 to 0.20% was measured at 70°C The results are given in Fig 1

The Freundlich adsorption equation (1) reduced to its simplest form may be written $x = kC^n$ or $\log x = \log k + n \log C$, where x is the amount of material adsorbed (millimoles per gram of carbon), C is the equilibrium concentration ($M \times 10^{-3}$), and k and n are experimentally determined constants Since a plot of log x vs log C should give a straight line, it is apparent that the adsorption of both the fatty acid and alkali components of these soaps over the concentration range investigated is in agreement with the Freundlich equation

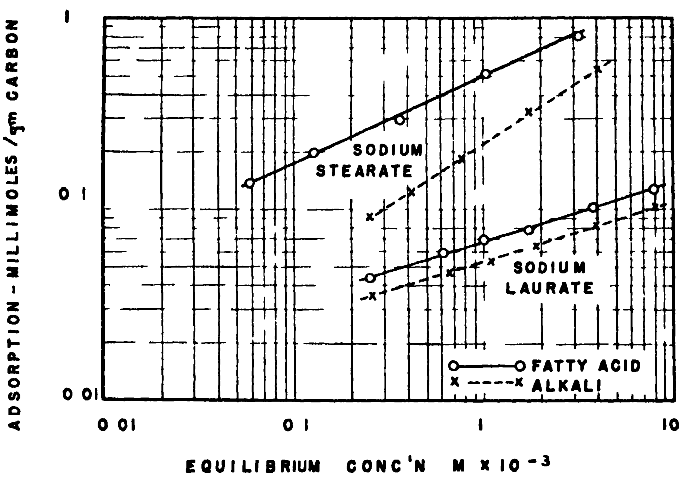

FIG 1 *Adsorption of soap components*

The constant k is a measure of the relative magnitude of the adsorption at a fixed equilibrium concentration, i e , in the present case k represents the adsorption in millimoles per gram of carbon when the equilibrium concentration is $1 \times 10^{-3}M$ The constant n is a measure of the rate at which adsorption increases with increasing equilibrium concentration The values of these constants (Table II) thus describe completely the adsorption of each component of the soaps for the particular adsorbing material and solvent used, and for the concentration range over which they are applicable

There is a greater adsorption of fatty acid than of alkali from the initially neutral* soap solution This is in agreement with the findings of Mikumo (6) for potassium oleate, and also accounts for the increased alkalinity of soap solutions after contact with carbon noted by Neville and Harris (9)

* *The term "neutral" soap is used to indicate equivalence of the fatty acid and alkali constituents of the soap The aqueous solution is of course alkaline in reaction owing to hydrolysis of the soap*

TABLE II

VALUES OF THE ADSORPTION CONSTANTS

Adsorbate	Component	Solvent	Equilibrium conc. range $M \times 10^{-3}$	k	n
Sod. laurate	Fatty acid	Water	0 25 - 8 0	0 068	0 31
Sod. laurate	Alkali	Water	0 25 - 8 0	0 053	0 31
Sod. stearate	Fatty acid	Water	0 06 - 3 2	0 195	0 45
Sod. stearate	Alkali	Water	0 25 - 4 0	0 216	0 61
Sod. hydroxide	- -	Water	0 68 23 4	0 140	0 29
Lauric acid		Alcohol	2 3 - 22 0	0 0095	0 93
Stearic acid		Alcohol	0 9 13 0	0 038	0 49

Effect of Chain Length of Soap on Adsorption

The adsorption of fatty acid and of alkali from soap solutions of initial concentration 0.1% was determined at 70°C. for the sodium soaps of lauric, myristic, palmitic, stearic, and oleic acids. The results are given in Fig. 2.

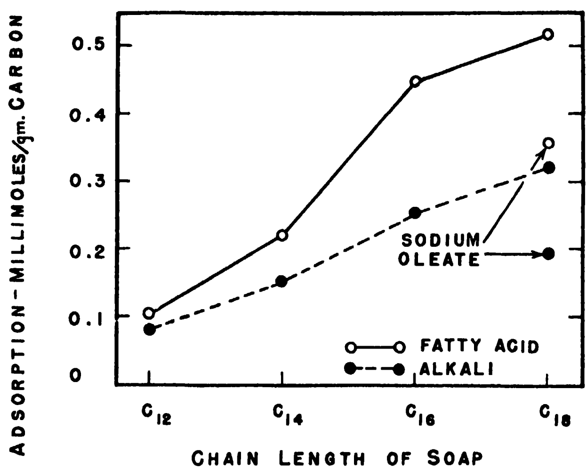

FIG. 2. *Effect of chain length of soap on adsorption.*

It will be observed that there is an increase in adsorption of both fatty acid and alkali with increasing chain length of the saturated soaps. There is also a greater adsorption of fatty acid than of alkali in every case, but this difference is greater for the longer chain soaps than for the shorter.

It is well known that the presence of the double bond in sodium oleate results in a shortening of the effective chain length. This is confirmed by the present data since the adsorption of both fatty acid and alkali from sodium oleate solutions lies between the corresponding adsorptions from sodium myristate and sodium palmitate. On the basis of these data the effective chain length of sodium oleate is approximately 15 carbon atoms.

Effect of Temperature on Adsorption

The effect of temperature on adsorption at 0.1% initial concentration was determined for the sodium soaps of lauric, stearic, and oleic acids (Table III). There appears to be a slight decrease in adsorption of both components of the soaps with increasing temperature, but the effect of temperature is small and in most cases scarcely greater than the probable error involved in its determination.

TABLE III

EFFECT OF TEMPERATURE ON ADSORPTION

Soap	Component	Adsorption, millimoles/gm carbon 30°C	50°C	70°C	80°C
Sod. laurate	Fatty acid	0.101	0.110	0.104	
Sod. laurate	Alkali	0.093	0.096	0.080	
Sod. stearate	Fatty acid			0.513	0.488
Sod. stearate	Alkali			0.321	0.307
Sod. oleate	Fatty acid	0.382	0.372	0.355	
Sod. oleate	Alkali	0.222	0.202	0.192	

*Adsorption of Alkali**

The adsorption of sodium hydroxide from aqueous solution at 70°C was measured at initial concentrations varying from 0.005 to 0.1%. The method was the same as was used for the determination of alkali adsorption from soap solutions, except that the ether extraction was omitted. It will be seen (Fig. 3

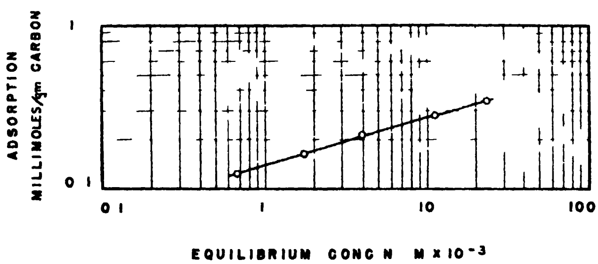

FIG. 3. *Adsorption of sodium hydroxide*

and Table II) that the adsorption of sodium hydroxide is in agreement with the Freundlich equation over the concentration range studied. This is in contrast to the findings of Miller (8) who reported no adsorption of sodium hydroxide from aqueous solutions by purified charcoal.

The disagreement between the present data and those of Miller can probably be attributed to the presence of materials other than chemically pure carbon contained in the carbon black. Miller has suggested that the discordant data

* *A second batch of standard Micronex was used for this and subsequent work. Adsorption values obtained with this material were somewhat higher than those obtained with the previously used material.*

relative to the adsorption of alkali by carbon reported in the literature prior to the time of his writing are due to the presence of adsorbed acids on the carbon, and that the observed reduction in concentration of the solution after contact with carbon is due to neutralization of these acids, rather than to true adsorption

However, since no attempt was made to purify the carbon black used in the present work, this material cannot be compared to the highly purified charcoals used by Miller While part of the observed consumption of alkali may possibly be due to neutralization of small amounts of acid contained in the carbon, the slope of the curve in Fig 3 indicates that adsorption of hydroxide by some constituent of the carbon black has taken place Had the consumption of alkali been due entirely to neutralization, the curve obtained would have been a straight line parallel to the concentration axis

This view was confirmed by attempts to measure the amount of acid contained in the carbon by the method given by Miller (8), in which a weighed amount of carbon is boiled with a known volume of standard sodium hydroxide solution, filtered, washed thoroughly, and the hydroxide in the filtrate titrated with standard acid It was found that the value for the amount of acid contained in the carbon increased with increasing concentration of the sodium hydroxide solution used This clearly indicates that the removal of hydroxide from solution is due, in part at least, to adsorption

Adsorption of "Unbalanced" Soaps

The term "unbalanced" is used to describe solutions in which the fatty acid and alkali components of the soap are not present in equivalent proportions For this work, batches of sodium laurate and sodium stearate were prepared containing approximately 15% excess fatty acid, i e , in the preparation of the soap only 85% of the fatty acid was neutralized with sodium hydroxide Solutions containing lower amounts of excess fatty acid and varying amounts of excess alkali were prepared by adding to a solution of the above "acid" soap the required amount of sodium hydroxide solution

Solutions containing any appreciable excess of fatty acid were quite cloudy owing to the presence of suspended fatty acid or acid soap, and on filtering, it was found that a small amount of the fatty acid (approximately 2% of the excess) was retained by the filter paper This would lead to some error in determining the concentration C_0 of the reference solution On the other hand, filtrates from these solutions after shaking with carbon were perfectly clear, and were found to contain an excess of alkali, indicating that all of the excess fatty acid had been removed by the carbon The loss on filtration of such solutions was shown previously to be negligible In view of these considerations, filtration of the reference solution was eliminated throughout this section of the work

The adsorption of fatty acid and alkali from sodium laurate and sodium stearate solutions at 70°C was measured for solutions containing initially

0.1% of neutral soap and varying amounts of excess fatty acid or of alkali. The results are given in Fig. 4.

In comparing the curves for fatty acid and alkali adsorption, it may be assumed that the lower of the two curves at any point on the abscissa represents the adsorption of neutral soap (or at least the adsorption of fatty acid and alkali in equivalent proportions), while the difference between the two curves represents the preferential adsorption of either fatty acid or alkali, depending on the relative positions of the two curves. On this basis it may be concluded that the adsorption of neutral soap is not influenced by the presence of varying amounts of excess fatty acid. It is probable that only the fatty acid actually in solution can influence the adsorption of neutral soap, and once the solubility limit has been reached, further additions of fatty acid have no effect. On the

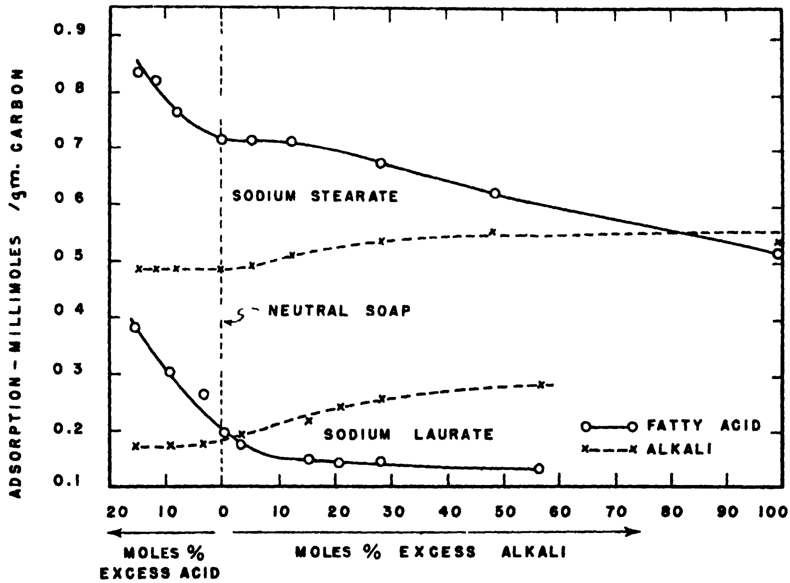

FIG. 1. *Adsorption of components of unbalanced soaps.*

other hand, the suspended fatty acid (or acid soap) is readily adsorbed by the carbon, as is shown by the rapid increase in adsorption with increasing amounts of excess fatty acid.

In the presence of increasing amounts of excess alkali, the alkali adsorption increases gradually while the fatty acid adsorption tends to decrease. In the case of sodium laurate the two curves cross at about 2 mole % excess alkali, but with sodium stearate a preferential adsorption of fatty acid is indicated until about 80 mole % excess alkali is reached.

Adsorption from Alcoholic Solution

In these experiments the soap was dissolved in freshly distilled 95% ethyl alcohol. The adsorption determinations were carried out as for aqueous

solutions except that after measurement of the aliquot of filtrate the alcohol was distilled off and was replaced by an equal volume of distilled water. The adsorption of sodium laurate at 0.1% initial concentration and of sodium stearate at 0.05 and 0.1% was determined at 25°C. A similar series of experiments was carried out in which absolute alcohol and dried reagents were used, and exposure to atmospheric moisture was limited to the filtration period. The results are given in Table IV, in which the corresponding values for aqueous solutions are also included.

TABLE IV

COMPARISON OF ADSORPTION OF SOAP FROM AQUEOUS AND ALCOHOLIC SOLUTION

Soap	Component	Initial conc., %	Adsorption, millimoles/gm. carbon		
			Aqueous solution	95% alcohol solution	Absolute alcohol solution
Sod. laurate	Fatty acid	0.1	0.195	0.011	
Sod. laurate	Alkali	0.1	0.182	0.135	
Sod. stearate	Fatty acid	0.05		0.025	0.026
Sod. stearate	Alkali	0.05		0.085	0.087
Sod. stearate	Fatty acid	0.1	0.719	0.036	0.032
Sod. stearate	Alkali	0.1	0.485	0.097	0.103

The data show that the adsorption of both fatty acid and alkali is considerably lower from alcoholic solution than from aqueous solution, particularly in the case of sodium stearate. Furthermore, the preferential adsorption of fatty acid observed with aqueous solutions does not occur with alcoholic solutions, there being, on the contrary, a preferential adsorption of alkali in the latter case.

The results obtained with absolute alcohol are not significantly different from those obtained with 95% alcohol, indicating that the presence of small amounts of water has no measurable effect on the adsorption.

The adsorption of free lauric and stearic acids from 95% alcohol solutions of varying initial concentrations was also determined at 25°C., the data being given in Table II and Fig. 5.

Discussion

Two possible mechanisms for the adsorption of soap from aqueous solution by carbon may be postulated, viz.: (*a*) neutral soap is not adsorbed as such, but the products of hydrolysis are adsorbed [this view is expressed by Miller (8) in relation to the adsorption of inorganic salts]; (*b*) neutral soap is adsorbed as such and, in addition, the hydrolytic products are also adsorbed, each adsorption taking place more or less independently.

If only the hydrolytic products are adsorbed, suppression of hydrolysis should lead to a marked reduction in adsorption. It was hoped that measurements of the adsorption of soap from alcoholic solutions might throw some light on this point since hydrolysis is completely suppressed in solutions containing 40% or more of ethyl alcohol (3, 11, 12). While it is true that a marked reduction in the adsorption of soap occurred when alcohol was used in place of water, it was found that the adsorption of free fatty acid from alcoholic solution was also very low (Fig. 5). It is probable, therefore, that the decreased adsorption of soap from alcoholic solutions as compared to that from aqueous solutions is not due entirely to the suppression of hydrolysis by alcohol.

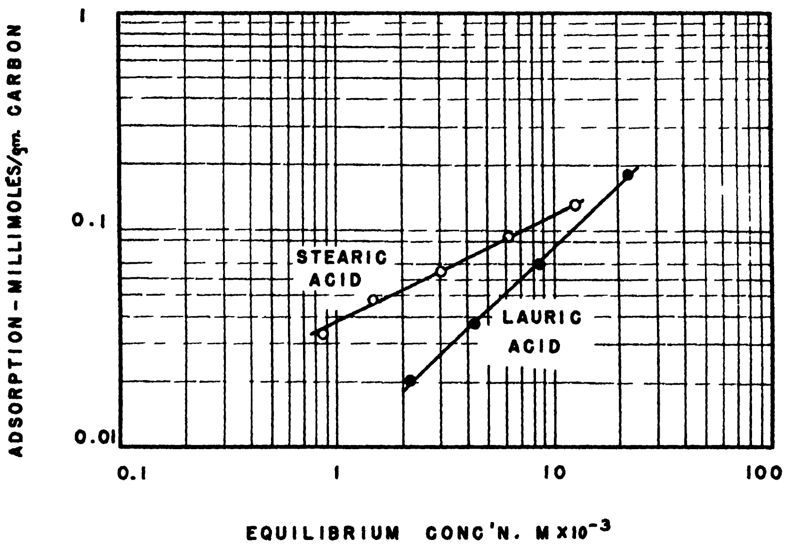

FIG. 5. *Adsorption of fatty acids from alcohol solution*

From adsorption measurements in aqueous solution (Fig. 4) it is apparent that an excess of free alkali causes a decrease in the adsorption of fatty acid. McBain and Martin (5) have concluded that the presence of 3 to 4% excess sodium hydroxide is sufficient to suppress completely the hydrolysis of sodium palmitate in 0.1% aqueous solution at 90°C. It is reasonable to assume that the decrease in fatty acid adsorption observed is due in part at least to the suppression of hydrolysis by the excess alkali, since neutral soap is probably adsorbed less readily than is the hydrolytic fatty acid (2). On the other hand, even in the presence of 100 moles % excess alkali there is still an appreciable adsorption of fatty acid, and it must therefore be concluded that this fatty acid is adsorbed in the form of neutral soap molecules. This indicates that the mechanism of adsorption from aqueous solution is a combination of adsorption of neutral soap and hydrolytic fatty acid. In the presence of increasing amounts of excess fatty acid the adsorption of neutral soap remains essentially constant whereas the adsorption of fatty acid increases rapidly

(Fig. 4). This would indicate that the adsorptions of the two species take place more or less independently of each other.

From measurements in alcoholic solutions Mikumo (7) found that the value of the constant n in the Freundlich equation was essentially constant for all soaps examined. On the other hand, the present data for aqueous solutions (Table II) indicate that the value of n varies with different soaps. The difference in the two cases may be attributed to the effect of hydrolysis. In the case of alcoholic solution, since hydrolysis is suppressed, the value of n is determined only by the adsorption behavior of the neutral soap. With aqueous solution the value of n for the fatty acid adsorption curve is dependent on the adsorptive characteristics of neutral soap, and also on those of the hydrolytic fatty acid. Since the degree of hydrolysis varies with different soaps, it is to be expected that the value of n will also vary.

Further confirmation of this view is to be found in the data shown in Fig. 2. If the alkali adsorption curve in this figure is taken to represent the adsorption of neutral soap and the difference between the two curves to represent the preferential adsorption of fatty acid, then it follows that not only does the total adsorption of fatty acid and alkali increase with increasing chain length, but the difference between the two, representing the adsorption of hydrolytic fatty acid, also increases with increasing chain length, i.e., with increasing degree of hydrolysis.

It is thus to be concluded that the second of the two mechanisms postulated is the correct one. The carbon particle with its adsorbed soap film may be likened to a micelle of acid soap of variable composition having a carbon particle as a nucleus. Whether this process is considered as adsorption of soap by the carbon or as "solubilization" of carbon by the soap would seem to be dependent only on the relative amounts of the two substances being considered.

Referring again to the adsorption measurements in alcoholic solution, it will be seen that the total adsorption is relatively low, and that there is a small but significant preferential adsorption of alkali. This suggests that some splitting of the soap molecule into its component parts must occur even in absolute alcohol solution. Theoretically this might be due to simple hydrolysis since traces of moisture were undoubtedly present in spite of attempts to maintain the system in as dry a condition as possible. However, hydrolysis is believed to be suppressed completely in alcohol solution and this claim is confirmed by the fact that adsorption values obtained using 95% and absolute alcohols as solvents were not significantly different. If the splitting of the soap molecule is to be attributed to reaction with water, the adsorption figures for solutions containing 5% of water should be noticeably different from those for solutions containing only a trace of water.

The other alternative is reaction with the alcohol itself, viz., alcoholysis. Such a reaction would have to take place to only a slight extent in order to

account for the experimental data, since the equilibrium would be displaced owing to adsorption of the reaction products. In order to explain the experimental data it would then be necessary to assume that sodium hydroxide is more readily adsorbed than either sodium stearate or ethyl stearate, from alcoholic solution.

From the data for fatty acid and alkali adsorption it is possible to calculate the composition of the adsorbed material in terms of the molar ratio of excess fatty acid to neutral soap (the neutral soap term may include, in addition to neutral soap, free fatty acid and sodium hydroxide, products of hydrolysis, in equivalent amounts). The effects of initial composition of the soap solution, chain length of the soap, and temperature, on the composition of the adsorbed

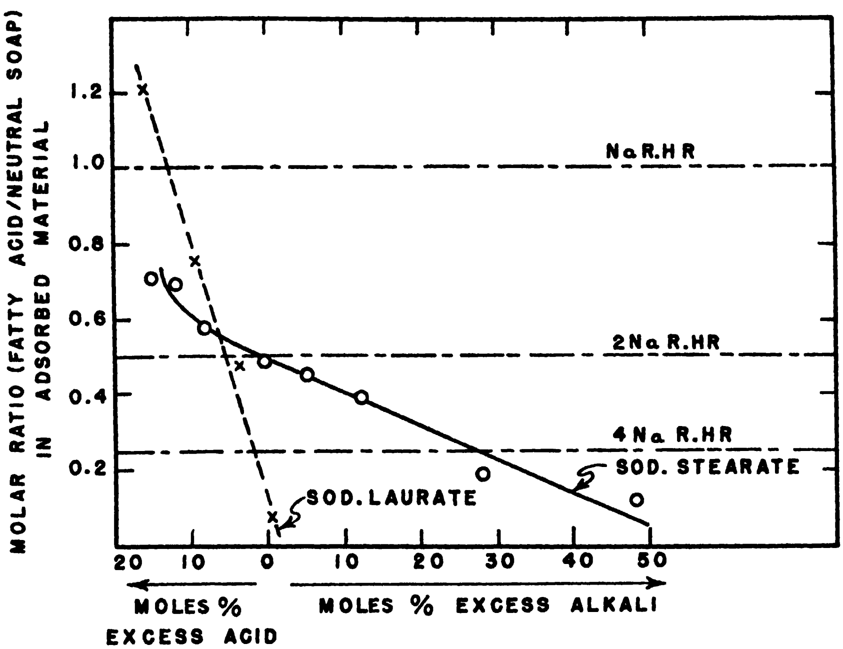

FIG. 6. *Composition of adsorbed material*

material are shown in Figs. 6, 7, and 8. From these data there appears to be no indication of the formation or adsorption of acid soaps of a constant composition. It is interesting to note (Fig. 6) that the addition of lauric acid to sodium laurate, which is a slightly hydrolyzed soap, causes a rapid change in the composition of the adsorbed material. On the other hand, the addition of stearic acid to sodium stearate causes a much smaller change in the composition of the adsorbed material. Sodium stearate is strongly hydrolyzed; consequently there is a considerable amount of hydrolytic fatty acid present in the initial solution and the addition of more fatty acid has much less effect than with sodium laurate, where the amount of hydrolytic fatty acid is low.

The effect of temperature on the composition of the adsorbed material (Fig. 7) can be explained on the basis of hydrolysis, since the degree of hydrolysis increases with increasing temperature (4).

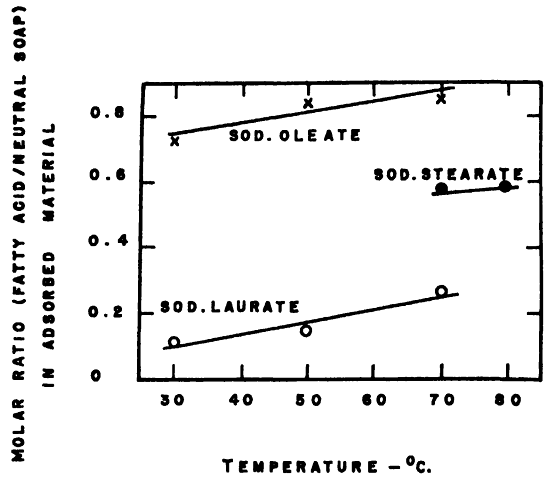

FIG. 7. *Effect of temperature on composition of adsorbed material.*

The data given in Fig. 8 may also be explained on the basis of hydrolysis. In general the degree of hydrolysis increases with increasing chain length of the soap, and consequently adsorbed films of the higher soaps contain a greater

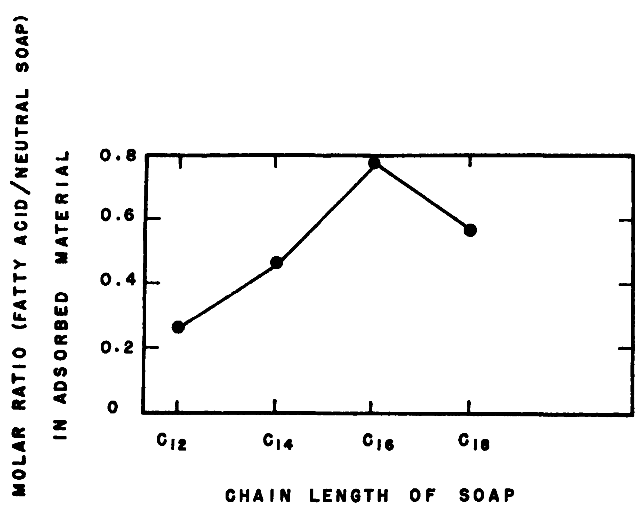

FIG. 8. *Effect of chain length of soap on composition of adsorbed material.*

proportion of free fatty acid than do those of the lower soaps. The explanation of the apparent discrepancy in the palmitate and/or stearate values is probably to be found in the hydrolytic behavior of these soaps. Under certain conditions

sodium palmitate may be more strongly hydrolyzed than sodium stearate, e.g., at 25°C. a 0.002 *N* solution of sodium palmitate is 15.8% hydrolyzed, whereas sodium stearate solution of the same concentration is only 10.0% hydrolyzed (4). While data are not available for the hydrolysis of these soaps at 70°C., it is conceivable that at the particular temperature and concentration employed the hydrolysis of sodium palmitate may exceed that of sodium stearate.

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COLLABORATIVE ANALYSIS OF WHEAT, OATS, AND BARLEY FOR THIAMINE AND RIBOFLAVIN[1]

By E. Y. Spencer,[2] A. D. Robinson,[3] L. W. McElroy,[4] J. Kastelic[5]

Abstract

In the analysis of wheat, oats, and barley for thiamine and riboflavin by three collaborating laboratories an attempt was made to reduce interlaboratory differences to a minimum by the establishment of a standardized procedure. The thiochrome and fluorometric methods were used for the thiamine and riboflavin determinations respectively. It was apparent that even after steps had been taken to standardize the assay procedures, small but consistent and significant interlaboratory errors existed. Calculations indicate that differences of the order of 10 to 12% in mean assay values were necessary before samples could be considered different with respect to their thiamine or riboflavin content.

Introduction

Experience has shown that different laboratories, analyzing the same samples of biological material for thiamine and riboflavin, may get results showing a wide variation. Thus, reports of the National Check Sample Committee of the American Association of Cereal Chemists (1, 4, 5) show that the mean values found by the co-operating laboratories ranged from 5.28 to 8.26 μgm. per gm. for thiamine in the six 1943-44 check samples, from 4.28 to 5.37 μgm. per gm. for six 1944-45 check samples, and from 3.09 to 5.31 μgm. per gm. for six 1946-47 samples. The results for riboflavin in the 1946-47 samples ranged from 1.77 to 3.76 μgm. per gm.

Obviously when such variations are possible, results from different laboratories cannot be readily compared. The laboratories of the Canadian prairie universities were conducting vitamin surveys of grains grown in their respective provinces, and it was desirable that the results should be comparable. It was thought that if the same methods were used in different laboratories, and if each step in the two procedures was standardized rigidly, it might be possible to obtain results agreeing much more closely. Accordingly, the three co-operating laboratories initiated the study, the results of which are reported herein.

Methods and Materials

The method adopted for the thiamine assay was essentially the thiochrome procedure as outlined by Hennessy (3). Incubation with takadiastase followed the acid digestion. The initial digestions were done in 100 ml. volumetric

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[2] *Associate Professor of Chemistry, University of Saskatchewan.*
[3] *Associate Professor of Chemistry, The University of Manitoba.*
[4] *Associate Professor of Animal Husbandry, University of Alberta.*
[5] *Formerly Biochemist, Nutrition Laboratory, University of Alberta.*

flasks to avoid possible loss in transferring the mixtures. Greater ease and uniformity of percolation were obtained when the adsorption columns were prepared by pouring Decalso into exchange tubes which had just been filled with water. The thiamine was removed from the Decalso by eluting with hot potassium chloride solution. The oxidation of the thiamine to thiochrome with alkaline ferricyanide was facilitated by injection of the oxidizing agent into the thiamine eluate by means of a hypodermic syringe.

Chemicals with low fluorescence were used to keep blank readings at a minimum. Several lots of anhydrous sodium sulphate were rejected for this reason. Initially, aliquots from the same batch of Decalso and quinine sulphate were used by the co-operating laboratories. New lots of chemicals were checked with the ones formerly used.

Calculations were made by comparing the sample readings with those for external standards, that is, an aliquot of pure thiamine hydrochloride solution, subjected to oxidation and extraction with isobutanol, but not to the earlier steps of the procedure. These standards were tested daily, with the weekly average being used for the final calculations. Duplicates were done on successive days. Assays which differed by more than 5% from the mean of that sample were repeated. Since exhaustive tests revealed that recovery of thiamine from samples using this procedure is only 91%, in an external standard, the results were therefore adjusted for 91% recovery. Each laboratory used a Coleman Electronic Photofluorometer, Model 12, for measurements. Readings of standard solutions were checked between laboratories.

The method adopted for the assay of riboflavin was essentially the fluorometric one reported by Andrews (2). Initial acid digestion was followed by takadiastase hydrolysis Further purification was obtained by adsorption of the riboflavin on Florisil The preparation of the adsorption columns was modified to the extent that a hot water suspension of Florisil was added to the exchange tubes. A measured volume—0 25 ml.—of ice-cold solution of sodium hydrosulphite and sodium bicarbonate was used instead of sodium hydrosulphite crystals. An external standard of riboflavin in pyridine – acetic acid solution was used for comparison, rather than one obtained by adding riboflavin to the sample. Duplicates were done on successive days. A slightly greater margin of error was allowed than was permitted for thiamine since the riboflavin content of cereals is considerably smaller.

In order to standardize a method for the three laboratories common samples of wheat, oats, and barley of the 1945 crop were used. These were ground in one of the laboratories and aliquots distributed. The collaborative method for thiamine and riboflavin was then employed to assay 59 wheat, 47 oat, and 46 barley samples of the 1946 crop which had been grown in the three provinces. These samples were obtained from University test plots, Experimental Farm and Illustration station plots as well as from Junior Grain Club plots, and were pure strains. They were widely distributed, being grown on dark brown,

black, light brown, and gray soil types. The samples were ground in the province of origin and portions distributed to the other two laboratories. Moisture was determined by the 130°C. air oven method.

Results and Discussion

Results are reported in micrograms per gram at a 13.5% moisture level. The mean values shown in Table I, obtained from the three laboratories, indicate the following range observed in thiamine and riboflavin content of samples of wheat, oats, and barley grown in different locations in the prairie provinces. There appears to be a high correlation between the protein and thiamine content. This is borne out by results from one of us (E.Y.S.) on a much larger number of wheat samples. Correlations in this last survey are also being made between thiamine and variety and soil type.

TABLE I

RANGE OF THIAMINE AND RIBOFLAVIN CONTENT OF CEREALS

Cereal	No. of samples	Thiamine, μgm./gm.	% Protein*	Riboflavin, μgm./gm.
Wheat	59	3.48 – 6.35	8.7 – 16.9	0.91 – 1.47
Oats	16	4.75 – 9.35	10.3 – 15.9	0.99 – 1.61
Barley	47	2.89 – 6.32	8.7 – 14.9	0.96 – 1.63

* *Protein values are for the respective samples containing the least and most thiamine.*

Table II indicates the mean, mean deviation, and standard deviation within laboratories and sum of differences from the mean of the three laboratories for the three cereals.

An analysis of variance for the thiamine and riboflavin data from the three laboratories is shown in Table III.

This analysis shows that, with the exception of thiamine in oats, the F values are highly significant for variance attributable to the results obtained at different laboratories.

Minimum significant sample and interlaboratory differences between samples and laboratories were calculated at the 5% level and are included in Table IV.

It was found that, for thiamine in wheat and barley, differences in the results obtained in laboratories B and C were not statistically significant, while those obtained at laboratory A were significantly lower. In the case of riboflavin, the results from laboratory A were significantly lower for wheat and oats, while, for riboflavin in barley, the results from laboratory C were significantly higher than those from the other two. It is thus apparent that even after steps were taken to standardize the assay procedures and, as far as possible, the equipment in the collaborating laboratories, small but consistent and significant interlaboratory errors existed. As indicated above and in Table II, this was

TABLE II
SUMMARY OF VITAMIN ASSAYS
μgm./gm.

	Thiamine assays				Riboflavin assays			
	Lab. *A*	Lab. *B*	Lab. *C*	Three labs.	Lab. *A*	Lab. *B*	Lab. *C*	Three labs.
Wheat								
Mean	4.41	4.79	4 73	4.64	1 08	1 17	1.15	1.13
Mean deviation	0.08	0.13	0.14		0 03	0.04	0.02	
St. deviation	0 44	0.54	0.56	0.57	0.08	0 15	0.11	0.15
Sum of differences from mean	−13.82	8 58	5.18		−3 35	2 49	0.95	
Oats								
Mean	6 86	6 86	6 95	6 89	1 27	1.32	1 33	1.31
Mean deviation	0 10	0 12	0.12		0 04	0 05	0 03	
St. deviation	1 45	1 28	1 36	1.37	0 18	0.12	0.19	0.14
Sum of differences from mean	−1 51	−1.21	2.77		−1 78	0.54	1.14	
Barley								
Mean	4 34	4.50	4 59	4 47	1 27	1 25	1 32	1.28
Mean deviation	0 08	0 12	0 10		0.04	0 05	0 02	
St. deviation	0.60	0 71	0 75	0 74	0 22	0 16	0 22	0.19
Sum of differences from mean	−7 00	1 55	5 55		−0 39	−1 55	1 94	

TABLE III
ANALYSIS OF VARIANCE

Variance due to	Thiamine		Riboflavin	
	Degrees of freedom	Mean square	Degrees of freedom	Mean square
Wheat				
Labs	2	5 01**	2	0.30**
Samples	58	1.29**	59	0 05**
Labs × samples	116	0.17**	118	0 013**
Error	177	0.052	180	0.004
Total	353		359	
Barley				
Labs	2	1 64**	2	0 13**
Samples	46	2 92**	46	0.20**
Labs × samples	92	0 11**	92	0 011**
Error	141.	0 041	141	0.005
Total	281		281	
Oats				
Labs	2	0 58	2	0.10**
Samples	45	10.99**	45	0.15**
Labs × samples	90	0.31**	90	0.02**
Error	138	0 047	138	0.005
Total	275		275	

Significant beyond the 1% level.

due largely to the fact that assay values obtained at one laboratory were, with the exception of those for thiamine in oats and riboflavin in barley, consistently lower than those obtained at the other two laboratories.

TABLE IV

MINIMUM SIGNIFICANT DIFFERENCES

	Thiamine			Riboflavin		
	Samples		Laboratories, μgm./gm.	Samples		Laboratories, μgm./gm.
	μgm./gm.	%		μgm./gm.	%	
Wheat	0 48	10 3	0 11	0 13	11 5	0.03
Oats	0 38	8 5	0.16	0 16	12 3	0 04
Barley	0 64	9 2	0.10	0 12	9 4	0 03

It is shown in Table III that the F values for variance due to samples were highly significant even though the variance for the interaction between laboratories and samples was used as error. This was anticipated, since the samples varied with respect to origin and variety.

Thus the results of this study, in which duplicate assays were done on successive days in three collaborating laboratories, show that after taking into account intralaboratory error and the interaction between laboratories and samples, differences of 8.5 to 10.3% and 9.4 to 12.3% were necessary before samples could be considered different with respect to content of thiamine or riboflavin respectively.

A direct comparison between results cited (1, 4, 5) and those reported here is difficult. The large range in thiamine content shown in Table I contributes a disproportional amount to the magnitude of the standard deviation so that the coefficient of variability as used in the 1946-47 report of the Check Sample Committee (1) cannot be employed for comparative purposes as a measure of precision. However, examination of the minimum significant differences in Table IV indicates that an improvement in precision by collaborating groups has been achieved.

Acknowledgment

The authors wish to thank particularly Dr. A. G. McCalla of the Department of Plant Science, University of Alberta and Prof. H. Van Vliet of the Department of Farm Management, University of Saskatchewan, for assistance in the statistical analysis. Particular thanks are also due Dr. A. Hoffer and Mr. M. W. Galgan of the University of Saskatchewan.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXXI. PILOT PLANT STUDIES ON THE FERMENTATION OF WHEAT BY *AEROBACILLUS POLYMYXA*[1]

By A. C. Blackwood,[2] J. A. Wheat,[3] J. D. Leslie,[3] G. A. Ledingham,[4] and F. J. Simpson[2]

Abstract

In this paper are described the construction and operation of a pilot plant in which whole wheat mashes were successfully fermented by *Aerobacillus polymyxa*. A yield of 8.9 lb. of *levo*-2,3-butanediol and 5.9 lb. of ethanol per bushel of wheat was obtained which is a fermentation efficiency of 90%. The best fermentations were obtained at 32°C. using a 15% mash buffered with calcium carbonate. Agitation increased the fermentation efficiency at 96 hr. but decreased the diol to ethanol ratio. Reduced pressure did not change the efficiency but markedly reduced the ratio of diol to ethanol. Aeration had little effect. The presence of contamination organisms was highly detrimental and it was necessary to sterilize the mash vessels and piping. Although a backstocking technique could be practised in the preparation of inoculum, frequent recourse to stock cultures or improved strains was found advisable for maintenance of high yields.

Introduction

Laboratory studies on the production of 2,3-butanediol (subsequently referred to as diol) by the fermentation of wheat with *Aerobacillus polymyxa* were begun in these laboratories in 1942. Keen interest in the chemical and physical properties of this four carbon compound and its possible commercial use as a precursor for butadiene and as an antifreeze (5, 6, 8, 10) made it advisable to continue production and recovery studies beyond the laboratory stage. Wartime shortages and unavoidable delays prevented operation of the pilot plant until early in 1944. A small scale production unit was, however, in operation before this time (11). The data and experience obtained were applied to the larger pilot plant.

The object of the work was to determine the yields obtainable under optimum pilot plant fermentation conditions, and to produce material for recovery studies. The basic fermentation requirements had been investigated and reported previously (1, 2, 3, 4, 12). Whole wheat, when sterilized and buffered, had been found to be a satisfactory substrate, and laboratory methods of preparation were modified for pilot plant work. Considerable difficulty was experienced in obtaining noncontaminated fermentations but methods of sterilizing the mash, cooker, fermenters, and piping and of maintaining them

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[2] *Bacteriologist, Industrial Utilization Investigations.*
[3] *Chemical Engineer, Industrial Utilization Investigations.*
[4] *Mycologist, Industrial Utilization Investigations.*

sterile were developed A vigorous strain from initial isolations was selected and throughout pilot plant work new selections from this and other strains were made The results of inoculum studies in the laboratory were applied to pilot plant work and adjusted to routine conditions When these basic requirements had been met the effects of various fermentation conditions were investigated This paper deals only with the fermentation aspects of the pilot plant study while an earlier paper (13) is concerned with recovery studies

Equipment

The equipment consisted of storage bins, grinding and weighing apparatus, slurrying equipment, a large and a small cooker, two progagators, two fermenters, and a beer well A mash cooler was available but was not always used

The storage bins were constructed of wood and sectioned to provide space for grain, malt, and calcium carbonate The grain was ground in a small Greey attrition mill with an adjustable grind and a capacity of 12 5 bu per hr Screen analyses of the ground grain showed 4% coarser than 10 mesh, 62% between 10 and 20 mesh, 22% between 20 and 40 mesh, and 12% finer than 40 mesh with 2% passing 100 mesh The weighing hopper of 1000 lb capacity was made of galvanized sheet metal with sloping sides Some of the ground grain stuck to the sides but a standard vibrating mechanism would eliminate this objectionable feature

A diagram of the cooking and fermenting equipment is given in Fig 1 The slurrying tank was approximately 2 ft in diameter and 2 5 ft high with a capacity of 50 gal * Agitation was provided by two 7 in propellers spaced 8 in apart driven at 383 r p m A 4 in screw conveyor rotating at 11 1 r p m carried the grain from the weighing hopper to the slurrying tank at a rate of 510 lb per hr Water was metered manually to the tank, the rate was measured by a rotameter and total flow by a rotary piston meter The resulting slurry was pumped from the tank to the tops of the cookers with an open impeller centrifugal pump

The cookers were upright cylindrical vessels made of mild steel Their conical bottoms were fitted with radial steam spargers with an additional sparger immediately above the bottom discharge valve The large cooker had a capacity of 800 gal It was equipped with a vertical rake agitator driven at 12 r p m with the rakes spaced at 12 in intervals in a spiral arrangement The slurry feed pipe extended some distance into the cooker to prevent the mash from splashing on the walls of the vessel above the liquid level The small cooker had a capacity of 50 gal and was fitted with a nozzle mounted propeller mixer, driven at 1725 r p m The cooked mash was blown by steam pressure through a pipe which extended from the bottom of the cookers, through the top, and then to the fermenters and propagators

* *Imperial gallons are used throughout.*

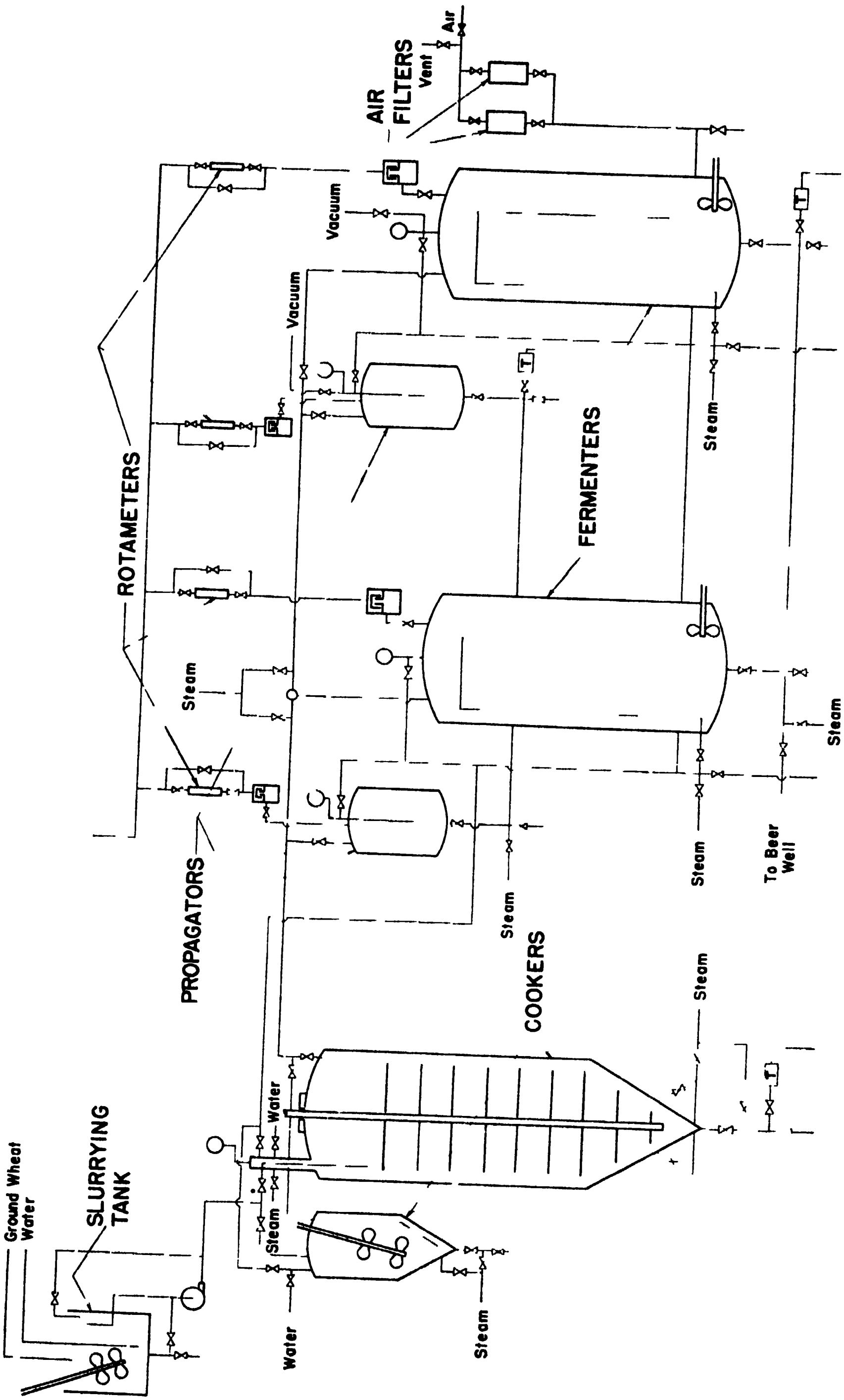

FIG 1 *Pilot plant mashing and fermenting equipment*

The two fermenters, identical in design, were of the deep vat, closed type. Their total capacity was about 750 gal., and a mash volume of about 450 gal. was used. Mash entered at the top and could be drawn off through a 2 in. discharge line at the bottom. Inoculum was added through a short 3/8 in. pipe at the top of the fermenter and samples were removed through a 3/8 in. line extending into the mash and curved downward above the fermenter. These are not shown in Fig. 1. A side entering agitator, located 1 ft. from the bottom of the cylindrical section, drove a three bladed, 12 in. diameter propeller located 1 ft. inside the tank. A seal cup beside the packing gland was filled with formalin to aid in preventing contamination. Sterile air entered the fermenters near the bottom, and various spargers could be connected. The final system adopted was to attach porous alumina aerators to the end of the air line shown in Fig. 1. These aerators had to be removed and cleaned after each fermentation in order to prevent them from plugging, and with the arrangement shown it was possible to disconnect the pipe and remove the aerators through the manhole. For gas discharge each fermenter had a separate water seal and scrubber.

The temperature was controlled by spraying thermostatically controlled water on the outside walls of the lower parts of the fermenters. The water was collected and recirculated. The fermenters had a minimum number of openings, and all connected pipes were lagged and kept under steam pressure when not in actual use. The tops of the fermenters were insulated to prevent heat loss and condensation.

The propagators were similar in design to the fermenters and each had a total capacity of 50 gal. They were supplied with steam, air, and temperature control using internal copper coils, but not with mechanical agitators. Each propagator had an individual water seal scrubber. These vessels were originally used to propagate inoculum for the fermenters but when it became evident that much smaller amounts of inoculum were as effective, the propagators were disconnected from the fermenters and used to test certain factors on a smaller scale.

The beer well was an open 1000 gal. tank equipped with a single paddle agitator. The fermented mash from both fermenters could be held in the beer well.

Auxiliary services to the plant provided water from the city mains, electrical power at 110, 220, and 550 v., and steam. A maximum steam pressure of 75 p.s.i. gauge was obtainable while the average was 50 p.s.i. gauge. Compressed air was available from either of two sources giving 50 and 100 p.s.i. gauge. Sterile air was obtained by passing compressed air through packed glass wool which was periodically steam sterilized. Reduced pressure was obtained with a small vacuum pump.

Experimental

Preparation of Slurry

The grain was elevated with a bucket elevator to the top floor and 650 lb. ground into the weighing hopper. The slurrying tank was filled with water and ground grain added from the hopper at a constant rate with the screw conveyor. Water was added to the tank at 4 gal. per min. and the liquid level in the tank was kept constant at the level of the overflow. The slurry that entered the overflow pipe was pumped to the top of the cooker. When all the grain had been added the slurrying tank was pumped out and rinsed with water. If calcium carbonate was to be added before sterilization it was mixed with the wheat in the hopper. If it was to be sterilized separately it was mixed with water in the slurrying tank and pumped to the small cooker.

Originally the ground grain was dumped directly from the hopper into 260 gal. of cold water, previously added to the cooker. The cover was replaced and cooking commenced. This system had a number of disadvantages. The grain dust spread rapidly and in addition to being a possible source of contamination this was very objectionable. In the cooker the fine particles settled on the walls above the water line, where they were cooked into a hard scale, providing another probable source of contamination. In addition, a poor mix was obtained as the grain clumped and tended to settle out, thus lowering sterilization efficiency. To overcome these difficulties the slurry tank was installed to provide rapid and thorough mixing.

Cooking and Sterilization

The most serious problem encountered was in obtaining consistently sterile cooks and uncontaminated fermentations. The thick, starch-gluten substrate complicated this problem. The most frequent cause of contamination was insufficient sterilization of the mash rather than the entrance of foreign organisms into the system after sterilization. The majority of the isolated contaminating organisms were spore formers. Only rarely were nonspore-forming contaminants encountered. James, Wilson, and Stark (7) report that whole wheat contains a natural flora that depends on the source, storage conditions, and grade. They found that the number of organisms was least with No. 1 Manitoba Northern, and progressively increased with successive lower grades with numbers ranging from 280,000 to 161,000,000 bacteria, 420 to 1870 fungi, and 6200 to 64,000 yeasts per gram. Over a period of time undesirable features and suspected sources of contamination were either removed or modified. The insertion of the slurry tank and changes in piping, which simplified connections but made the plant less versatile, solved the greater part of the problem.

To liquefy the thick mash, 2 lb. of ground malt was added. Initially, the malt was added to the slurry in the cooker and the temperature held at 70°C. for 20 min. before sterilizing. The final method adopted was to add the malt at the beginning of the slurrying operations, and, when these were complete,

to heat immediately to the sterilization temperature. Both methods gave a satisfactory reduction in viscosity but the latter was much simpler.

To heat the mash, steam was forced through the spargers at the bottom of the cooker. The temperature was followed on a recording thermometer. When all the air had been expelled from the cooker the vent valve was closed and the mash heated to the sterilization temperature. In test operations, 25 lb. of calcium carbonate was added to the mash and the whole heated to temperatures of 100°, 115°, 120°, and 125°C. for 1/2, 1, and 1 1/2 hr. The lower temperatures and shorter periods produced nonsterile mashes while higher temperatures and longer times produced caramelized mashes which fermented slowly or not at all. Cooking the mash at 115°C. for one hour appeared to be most suitable but even so four out of ten successive cooks were not sterile. Caramelized compounds are known to be more readily formed at alkaline pH levels. The pH of the mash sterilized with calcium carbonate was found to be 7.0 or slightly higher, while that of the grain slurry alone was approximately 6.0. By sterilizing the calcium carbonate separately the grain could be heated at 120°C. for one hour without observable caramelization. This treatment produced consistently sterile mashes and with a few exceptions subsequent contaminations were traceable to other sources. The lower grades of wheat were utilized for the fermentation, and it was thought that if exposing the grain to ultraviolet light would reduce the numbers, especially the spore load, sterile mashes might be obtainable with shorter cooking periods. Whole wheat was passed over a polished vibrating plate 4 ft. long at the rate of 10 lb. per min. and subjected to radiation from four 18 in. G.E. germicidal lamps. A reduction in the spore count from 3500 to 250 per gram was obtained. The grain, however, still had to be ground, weighed, and slurried before it entered the cooker, having ample opportunity to become reinfected. After grinding and weighing operations the spore count had increased to 1000 per gram. Although irradiating the ground grain immediately before slurrying was recognized as advantageous, it was not considered practical because of the flour and grain dust.

With irradiated grain a reduction of 15 min. in cooking time was possible but a further reduction resulted in a contaminated cook. No detrimental effect on the fermentation appeared to result from the action of ultraviolet light on the grain with the three treated cooks tested.

Prior to slurry operations a fermenter was closed and sterilized with steam at 20 to 30 p.s.i. gauge. Steam was bled from all openings to ensure that air and condensate were removed. One and a half to two hours was sufficient time for sterilization. When the mash had been sterilized for the proper time it was blown over with steam pressure to the fermenters. The fermenter was cooled with cold water during the transfer and its pressure kept low. A sudden rise in fermenter pressure indicated that all the mash had come over from the cooker. The mash lines were immediately flushed with steam and again put under pressure. Steam pressure was maintained in the connecting line at the bottom of the fermenters at all times except when it was used to transfer mash

While the mash cooled, sterile air was bled into the fermenter to maintain a positive pressure.

When the mash reached a temperature of 32°C., 25 lb. of calcium carbonate, previously slurried with 25 gal. of water and sterilized in the small cooker at 120°C. for one hour, was transferred to the fermenter in much the same manner as the mash. The fermenter temperature was then automatically controlled at 32°C. A low positive pressure was maintained until just prior to inoculation when the pressure was reduced to atmospheric and the inoculum added aseptically. As a check on operational technique the mash was allowed to incubate for 12 to 18 hr. before inoculation. Any contaminants then had an opportunity to multiply and could be easily detected. After inoculation, the fermentation proceeded at atmospheric pressure under controlled conditions. When the fermentation was complete, it was discharged into the beer well where it was held pending recovery operations.

Selection of Strain and Preparation of Inoculum

The cultures that were previously isolated and found to be good producers under laboratory conditions (12) were used in the pilot plant. Variations between the strains were marked and it was found advisable to reselect and test periodically. Selections from strain C12 (3) were used with good results in the pilot plant over a long period of time.

The cultures were stored at 3°C. on wheat agar slants, on slants under mineral oil, in sterilized soil, and at room temperature after lyophilization. All the methods appear to be equally satisfactory, but the mineral oil technique, because of its good preservation properties and simplicity, was finally adopted as routine. With this method an active culture was always available.

Heat shocking of sporulated cultures was tried but the results obtained with this treatment were somewhat erratic and the general trend appeared to be toward slightly lower yields. An attempt to acclimatize the organisms to diol and thus improve the yield was not successful. Five strains were incubated for 96 hr. periods in 15% wheat mashes containing 2% diol and in mashes containing increasing amounts of diol of 1% per transfer. After a series of 10 transfers a comparison with the original cultures of a normal 15% wheat mash was made. With the treated cultures the diol–ethanol ratio was raised from 1.3 to 2.3, but the combined yield was reduced from 4.2 to 3.6% products.

The original inoculation scheme involved three serial transfers from slant to propagator adding 6 liters of inoculum to 30 gal. of propagator mash. The mash was prepared in a manner similar to that described for the fermentation. After a 24 hr. incubation period this was transferred to the fermenter. The scheme gave an active inoculum which represented about 7% of the mash.

Laboratory tests (4) demonstrated that the amount of inoculum could be varied from 0.01 to 10% without affecting the yield and time required to complete the fermentation, although it did control the initial rate. In the pilot plant, adding inoculum at levels of 0.2, 0.1, and 0.05% gave completely

satisfactory results. The use of this low amount of inoculum is of importance in plant design as it eliminates large propagator equipment. On the above basis only 10 to 20 gal. of inoculum would be required for a 20,000 gal. fermenter. The practice adopted in the pilot plant was to add 2 liters of inoculum to the fermenter from a 4 liter aspirator bottle with an attached rubber hose and a metal guard tip which fitted into a 3/8 in. pipe on the fermenter.

The inoculum was prepared from agar slants by three 24 hr. stages. Transfers were made to 10 ml. of medium, to 200 ml., and finally to the 2000 ml. used to inoculate the fermenter. A backstocking technique was practised in the 200 ml. stage. Although backstocking through a series of six transfers had previously been found to give consistent yields (4), it was observed in the pilot plant that after a number of fermentations the yields and efficiencies decreased. In a supplementary laboratory study and under somewhat different conditions from the previous one, five strains were backstocked through 11 serial transfers and the diol and alcohol yields recorded after each transfer. A 15% mash distributed in 300 ml. amounts in 500 ml. Erlenmeyers was used with an incubation period of 96 hr. between transfers. On the eighth and ninth transfer the yields were observed to decline (Table I). Thus, in pilot plant operations, recourse was frequently made to stock cultures or to improved strains obtained by selecting and testing colonies from streak plates of fermenter samples.

TABLE I

THE EFFECT OF BACKSTOCKING IN 15% GRAIN MASHES

Backstock	Yield, %: Diol	Ethanol	Total products
1	2.22	1.10	3.62
2	2.30	1.43	3.73
3	2.16	1.37	3.53
4	2.40	1.47	3.87
5	2.50	1.33	3.83
6	2.20	1.36	3.56
7	2.24	1.28	3.52
8	1.99	1.08	3.07
9	2.04	1.09	3.13
10	1.94	1.06	3.10
11	1.92	1.10	3.02

The inoculating medium consisted of 1% ground wheat, 3% starch, 1.5% yeast extract, and 1% calcium carbonate. On this medium 500 million organisms per milliliter as estimated by direct count with a Petroff–Hauser plate were obtained after an incubation period of 24 hr. Malt sprouts or shorts offer a good commercial substitute for yeast extract as the added nutrient. Where no nutrient is added, growth is slower and numbers are much lower at 24 hr. The calcium carbonate may be omitted if the incubation period is not longer than 24 hr.

Fermentation

The effect of agitation, aeration, and reduced pressure on the yield and rate of fermentation was studied in the pilot plant. These factors had previously been studied in the laboratory (1, 3). It was shown that any treatment that assisted the escape of carbon dioxide increased the initial rate of fermentation with only a slight effect on the degree of completion at 96 hr. Thus a high surface–volume ratio, agitation, reduced pressure, and aeration with air, oxygen, nitrogen, or hydrogen increased the initial rate, while conducting the fermentation in an atmosphere of carbon dioxide decreased the initial rate. Aerobic conditions, such as a high surface–volume ratio, and aeration with air or oxygen increased the diol–ethanol ratio, while anaerobic conditions, such as reduced pressure and aeration with nitrogen, hydrogen, or carbon dioxide, decreased the ratio. The pH level of the fermentation in the range 5.8 to 7.0 was found (2) to have little effect on the yield or product ratio.

During the fermentation, samples were taken at 24-hr. intervals. Ethanol and diol analyses and a microscopic examination were made and the pH determined. The fermentation efficiency, ratio of diol to ethanol, yield of diol and ethanol in pounds per bushel, and relative value of the liquid products were calculated for noncontaminated fermentations from the 96 hr. analyses. The total weights of diol and ethanol in the fermented mash were calculated from the formulas given by Leslie and Castagne (9). The theoretical yield of diol plus ethanol is considered as one-half of the weight of glucose formed from the starch, and the fermentation efficiency is calculated as the actual yield of diol plus ethanol divided by the theoretical yield. The cost estimates described in a previous paper (13) established the cost of diol at about three times the selling price of ethanol. The relative value of the fermentation products is therefore calculated by multiplying the diol yield in pounds per bushel by three and adding the yield of ethanol. The average values obtained in a series of fermentations showed that the fermentations were 60 to 70% complete at 48 hr., 80% at 72 hr., and 90% at 96 hr. The pH was found to drop from 6.5 to 5.7 in the first 24 hr. with a final pH of 5.3 to 5.5.

The effect of agitation on the fermentation is shown by the results given in Table II. The effect of increasing the time of agitation is to increase the efficiency and to decrease the ratio of diol to ethanol. Twenty-four hours' agitation increases the efficiency appreciably but has only a small effect on the ratio. Agitation for 48 hr. reduces the ratio but does not increase the efficiency. The results for 72 and 96 hr. agitation showed only small differences so they have been combined. Continuous agitation for 96 hr. gives the products with the highest relative value but the difference is small.

The effect of reduced pressure is shown by the data in Table III. Most of the data are based on a single fermentation and hence definite conclusions cannot be drawn. The first portion of Table III gives the effect of increasing time of vacuum on fermentations agitated for 96 hr. The efficiencies vary considerably but the ratio and relative value tend to decrease. The second

TABLE II

THE EFFECT OF AGITATION ON THE FERMENTATION

Time of agitation, hr.	No. of runs	Efficiency,* %	Lb. per bushel		Ratio	Value*
			Diol	Ethanol		
0	19	85 0	8 50	5 52	1 54	31 0
24	8	88 2	8 73	5 83	1 49	32 0
48	5	87 3	8 38	6 01	1 39	31.2
72-96	11	92 8	8 65	6 65	1 30	32 6

* *See text for method of calculation.*

TABLE III

THE EFFECT OF REDUCED PRESSURE (15 IN. OF MERCURY VACUUM) ON THE FERMENTATION

Length of treatment, hr.	Time of agitation, hr.	No. of runs	Efficiency,* %	Lb. per bushel		Ratio	Value*
				Diol	Ethanol		
0	96	11	92 8	8 65	6 65	1 30	32 6
12	96	1	84 5	7 98	5 95	1 34	31 9
24	96	1	75 2	6 96	5 44	1 28	26 5
48	96	1	87 7	7 08	7 37	0 96	28 8
0	24	8	88 2	8 73	5 83	1 49	32 0
24	24	1	91 7	9 07	6 05	1 50	33 2

* *See text for method of calculation.*

TABLE IV

THE EFFECT OF AERATION ON THE FERMENTATION

Aeration		Agitation time, hr.	No. of runs	Efficiency,* %	Lb. per bu.		Ratio	Value*
Rate, c.f.m. per 1000 gal.	Time, hr.				Diol	Ethanol		
0	0	72-96	11	92 8	8 65	6 65	1 30	32 6
3.5	72-96	72-96	4	93 4	9 57	5 83	1 64	34 5
7 0	96	96	1	80 1	10 71	2 50	4 28	35 3
0	0	24	8	88 2	8 73	5 83	1 49	32.0
4 0	24	24	2	84 9	8 10	5 90	1 38	30 3
0	0	48	5	87 3	8 38	6 01	1 39	31 2
4 0	48	48	1	88 4	8 52	6 05	1 41	31 2

* *See text for method of calculation.*

portion of the table gives the effect of 24 hr. vacuum applied to fermentations agitated for 24 hr. The efficiency is increased slightly with only a small effect on the ratio.

Aeration data obtained with porous alumina aerators are given in Table IV. All fermentations were agitated throughout the aeration period. Aeration for 72 to 96 hr. increases the efficiency and ratio, giving a higher relative value. Aeration at a rate of 7.0 c.f.m. per 1000 gal. for 96 hr. caused a loss of ethanol, so that the efficiency is low and the ratio high. In spite of the loss of ethanol the relative value of the products is very high. Aeration for 24 or 48 hr. has only a slight effect on the efficiency and ratio.

Discussion

From the results given in Tables II – IV it is not possible to specify the best conditions for fermentations in much larger fermenters. The aeration results are not conclusive because of the small number of fermentations. However, the effect of aeration is less marked in the pilot plant than on a laboratory scale, so it may be concluded that the effect would be even less in large fermenters. Thus, it is not likely that increased yield of diol or saving of fermentation capacity would pay for the increased power requirements and the high initial cost of installing air compressors and aeration equipment. This also applies to the application of reduced pressure.

The installation of agitators would be advisable to facilitate removing the mash and for maintaining a constant and uniform temperature. If the cooked mash were to be cooled in the fermenters, agitation would be necessary. Thus an increased yield resulting from agitation would have to pay for only a portion of the power consumption in order to be justified. By installing an agitator with a low circulation rate and little shear the initial cost could be kept down. This might give the same effect and same power cost over a 72 or 96 hr. period as a larger agitator over a 24 hr. period.

Based on the results of Table II, a probable efficiency of 90% and a diol-to-ethanol ratio of 1.5 were used for subsequent cost estimates.

Acknowledgments

The authors wish to express their appreciation for the generous support and encouragement given this project by Dr. W. H. Cook, Director of the Division of Applied Biology. Of those who contributed to the design and operation of the pilot plant, Dr. G. A. Adams, D. Rose, W. S. King, and I. M Miller deserve special thanks. Acknowledgment is also made for the co-operation and invaluable assistance given by the technical and maintenance staff.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

VIII. THE CAUSES OF THE ANTIKNOCK PROPERTY OF RICH MIXTURES[1]

By R. O. King,[2] W. A. Wallace,[3] E. J. Durand[4]

Abstract

The engine experiments of this Part are a sequel to those of Part VII showing that enrichment of a pentane-air mixture accelerates oxidation at end gas temperatures to the antiknock substances, steam, and the carbon oxides. The corresponding antiknock effect in an engine is increased by cooling if enrichment of the mixture leads to an increase in the proportion of the fuel admitted to the engine as liquid. The engine experiments were therefore made using two fuels, *n*-pentane and a commercial fuel "S", containing high boiling point constituents. The pentane could be vaporized prior to admission to the engine and the antiknock effect due to cooling eliminated. Thus, two concurrent antiknock effects were obtained on enriching the fuel-air mixture—one due to cooling, if the fuel were admitted to the engine in part as liquid, and the other to the consequent increase in the velocity of the heterogeneous oxidation reaction in the end gas. It was also shown by the experiments of Part VII that the oxidation of rich mixtures at end gas temperatures, to steam and carbon dioxide, was greatly accelerated when iron carbonyl was added to the fuel. Similarly, the engine experiments of this Part show that the antiknock effect of enriching the fuel-air mixture is greatly enhanced when iron carbonyl is added to the fuel.

Introduction

It has long been known that the tendency of a particular fuel-air mixture to detonate in an engine reaches a maximum for a critical mixture strength and that both weaker and richer mixtures possess antiknock properties.

When using ordinary gasolines, maximum power is obtained when the mixture with air is somewhat on the rich side of the critical mixture, and a further substantial increase of mixture strength permits the use of relatively high compression ratios without detonation, though at some sacrifice of economy. Alternatively, compression ratio being fixed, as in practice, the use of rich mixtures makes possible an increase of charge density by supercharging without giving rise to the detonation which would otherwise limit the consequent power increase. Thus the fuel for supercharged aero engines is now required to give a specified increase in antiknock value, designated as "mixture response", for a particular increase in mixture strength.

The antiknock property of rich mixtures is inconsistent with currently accepted views that detonation or knocking combustion is due to an oxidation

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Contribution by Defence Research Board (Canada) and the Department of Mechanical Engineering, University of Toronto, Toronto, Ont.
[2] *Research Scientist, Naval Division, Defence Research Board, and Special Lecturer, Faculty of Applied Science, University of Toronto; lately Director of Scientific Research and Development Royal Canadian Navy.*
[3] *Lecturer in the Department of Mechanical Engineering, University of Toronto.*
[4] *Instructor in Mechanical Engineering, University of Toronto.*

reaction of the chain type, beginning with the formation of organic peroxides and proceeding to explosion in a homogeneous mixture, and that metallic antiknocks act by breaking the reaction chains. Organic peroxides are formed most readily in rich mixtures (2, p. 211) and if the antiknocks acted by destroying them or in any other way breaking the chains, the efficacy of a particular concentration of antiknock would diminish with increase of mixture strength. The opposite effect is observed in practice.

The antiknock property of rich mixtures has accordingly been given scant attention in attempts to apply chain reaction theory to oxidation as it occurs in an engine and the few available references are to the cooling effect. Thus Callendar (3, p. 511) explains that overrich mixtures reduce detonation by retarding ignition and lowering the engine temperature. Egerton (5, p. 2911) after mentioning the effect of enrichment of the mixture to increase rate of oxidation, which on the basis of his chain reaction theory would *promote* detonation, attempts to dispose of the anomalous antiknock property by suggesting that the proknock effect due to oxidation is offset by an antiknock effect due to cooling. Campbell, Lovell, and Boyd (4) describe experiments showing the importance of mixture strength in respect of the rating of fuels for antiknock value but do not attempt an explanation of the observed effects. Finally, Beatty and Edgar (1) in a lengthy review of "The theory of knock in internal combustion engines", describing in detail the factors influencing the promotion or prevention of the effect, make no mention of the antiknock effect due to enrichment of the mixture or the increase in the efficacy of the metallic antiknocks when used in rich mixtures; both effects are in contradiction to the chain reaction theories advanced.

Plan and Scope of the Experiments

Ordinary liquid fuels are more or less "atomized" in the carburetor of an Otto cycle engine. Vaporization requires the addition of heat and occurs mainly in the heated induction system and in the hot cylinder, where it is assisted by the hot residual gas. Any antiknock effect due to cooling by the fuel–air mixture is caused solely by the vaporization of the fraction of the fuel entering the cylinder as liquid. Experiments were planned accordingly, using two fuels, technical grade *n*-pentane and fuel "S". The initial boiling point of the pentane was 95°F.; 90% was recovered at 96.4°F. and 95% at 97.4°F., the end point. The initial boiling point of fuel S was 85°F. and 97% was recovered at 429°F., the end point (see Fig. 1). Distillations were in accordance with A.S.T.M. procedure, D86—46.

The pentane even in rich mixtures with air could be vaporized prior to admission to the cylinder and any antiknock effect then observed on enrichment of the mixture could not be due to cooling. Fuel S could be admitted almost entirely as liquid or could be vaporized in part only with the means available, prior to admission to the cylinder. Thus by using the two fuels and varying the rate of heat addition to the mixtures with air, conditions could be

obtained in which nearly all of the fuel could be admitted to the engine as vapor or nearly all as liquid, and the consequent effects on detonation determined by varying the compression ratio to maintain a standard knock intensity.

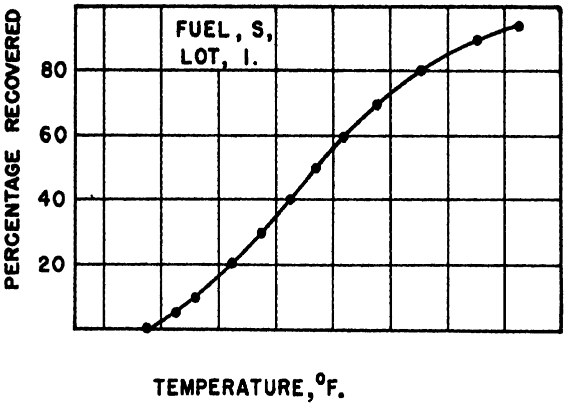

FIG. 1. *Distillation range, Fuel S, Lot 1.*

The scope of the experiments was extended to determine the antiknock effect of enrichment of mixtures with air of fuel S containing iron carbonyl in concentrations extending to 1.0 cc. per liter.

Experimental Arrangements

A standard C.F.R. unsupercharged variable compression engine was used for the experiments. The bore and stroke are 3.25 in. and 4.50 in. respectively and the compression ratio can be varied from 4 to 10 : 1. The engine is in universal use and further details need not be given although certain special arrangements require description.

Engine Cooling

The standard evaporative arrangement for maintaining the jacket water at a constant temperature of 212°F. was on occasion replaced by a cold tap water circulation, the flow being regulated manually to maintain any desired lower temperature.

Mixture Strength Regulation

The float chamber is flexibly connected to the carburetor, and mixture strength is varied by varying the height. When the chamber is in the "up" position, the surface of the fuel in it is level with the fuel opening into the carburetor throat, and maximum mixture strength is obtained. When the chamber is in the "down" position, the fuel level is 3.0 in. lower and mixture strength is generally too weak for engine operation. The rate of fuel consumption at a particular engine speed then depends on float chamber level, the density and velocity of the air passing through the carburetor throat, the vapor pressure of the fuel, and the diameter of a flow control orifice fitted in the fuel line from the float chamber to the carburetor.

Measurement of Mixture Strength

The C.F.R. knock testing engine is not provided with a fuel flow meter. The mixture strength required for maximum knock having a critical value for any particular fuel, the percentage variation from it can be calculated if corresponding rates of fuel consumption be measured. Fuel flow metering arrangements made accordingly were based on observations of the time required for the consumption of a particular weight of fuel, and were similar to those of the Waukesha Motor Co. (8).

Mixture Temperature and Fuel Vaporization

The air supply to the carburetor was at room temperature and humidity was not controlled. The mixture of air and liquid fuel passed from the carburetor through a heating chamber to the inlet passageway in the engine head. A requirement of the C.F.R. "motor method" of knock testing is that the combustible mixture be raised to a temperature of 300°F. prior to admission to the engine, and it is necessary in order to avoid oxidation and possible pre-ignition that the mixture be brought into contact with moderately heated surfaces of relatively large area. The effective length of the heating chamber is 7.0 in. and the inside diameter 1.72 in. Two electric heating elements each 6.75 in. long, 1.06 in. wide and 0.36 in. thick are fitted in the chamber. The area of electrically heated surface is 39.5 sq. in. and that of the surrounding surface heated by radiation is 44 sq. in. There is, in addition, about 12 sq. in. of heated induction passageway surface in the cylinder head leading to the inlet valve.

It is a requirement of the scheme of the experiments that *n*-pentane be completely vaporized prior to admission to the cylinder when the mixture temperature is 300°F. and the jacket temperature 212°F. The heat input in these conditions was 47 B.t.u. per min. and of this 6 were required to vaporize the pentane at the maximum rate of consumption and 26 to heat the air, leaving a balance of 15 for radiation and conduction. It is a fair assumption, therefore, that the mixture heating arrangements suffice to vaporize completely the *n*-pentane in a mixture with air raised to 300°F. even in the time available, when it is considered that the volume of the heater space was approximately 50% of that of the stroke volume of the engine and that the vapor pressure of the pentane at the laboratory temperature at the time of the experiments was approximately 600 mm. of mercury.

Mixture temperatures given later and on relevant graphs were as indicated by a mercury-in-glass thermometer with the bulb in a pocket in the short passageway from the heating chamber to the inlet port of the engine.

Ignition Timing

The standard C.F.R. method of changing ignition timing with change of compression ratio was used and timing was varied from 33.5° advance at 4:1 compression ratio to 14.7° advance at 10:1, but the relation is not linear as shown by the graph of Fig. 2.

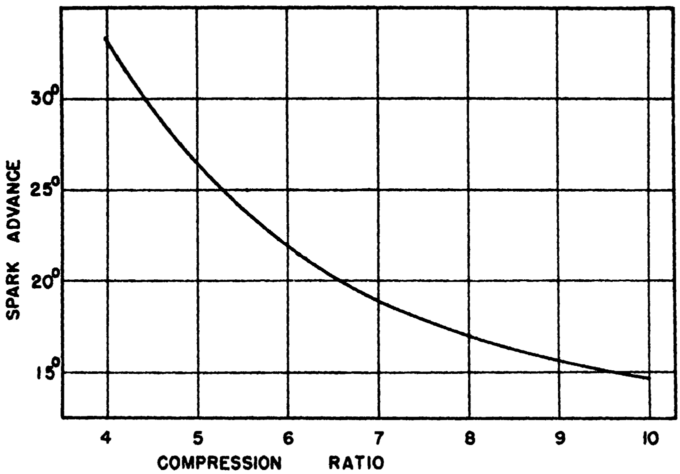

FIG 2. *Variation of spark advance with compression ratio, C.F.R engine.*

Engine Speed

The C.F.R. engine is usually arranged to drive a synchronous generator connected to an a-c. supply of constant frequency. The engine speed is thus maintained constant regardless of power output. The C F.R. engine used for the experiments was connected by a belt drive to a d-c. generator and electrical output absorbed by a resistor bank. The engine speed was maintained at *900 r p.m. for all of the experiments* by manual regulation of the field resistance.

Standard Knock Intensity

The C.F.R. bouncing pin device and knock meter were used for determinations of an arbitrarily chosen "standard knock intensity" equivalent to that obtained in C.F.R. knock testing practice when using a standard 75 octane fuel at a compression ratio of 5 26. The calibration of the bouncing pin was always checked accordingly before starting experiments.

Inlet Valve

A shrouded inlet valve is fitted as standard to the C.F.R. engine. The valve imparts a swirl to the entering mixture but the consequent restriction reduces volumetric efficiency. It was replaced by a spare exhaust valve of the common tulip shaped variety.

Lubrication

The engine was lubricated with a commercial brand of oil, S.A.E. 30, without "additives". The oil in the crank case was maintained at temperatures between 120° and 130°F., by a manually controlled electric heater.

Experimental Results

Experiments were made with a jacket water temperature of 212°F. obtained by the evaporative cooling method already mentioned and with a jacket water temperature of 150°F. obtained by the circulation of tap water, as indicated

by a thermometer with the bulb in a pocket in the circulating water *outlet* of the cylinder head. The term "jacket temperature" is used for convenience to describe temperature conditions as above. It will be understood that the corresponding cylinder wall and combustion space surfaces are higher to an unknown extent, depending on variable heat transfer factors.

The rate of fuel consumption was varied from the minimum at which the engine would run steadily to the maximum obtainable with the C.F.R. 0.027

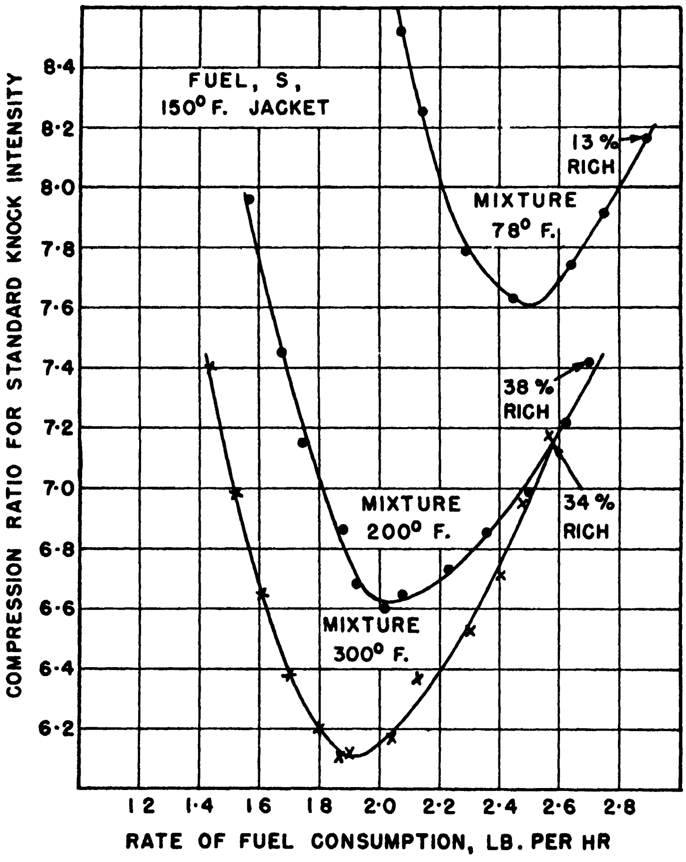

FIG. 3. *Fuel S, Lot 1. 150°F jacket temperature.*

in. dia. fuel control orifice usually fitted for use with hydrocarbon fuels. Observations were thus obtained of the antiknock effects due to weakening as well as to enriching the mixture. The use of weak mixtures was of beneficial effect in burning the carbon deposited during previous running of very rich mixtures. Thus when the experiments were completed, the combustion space was found to be remarkably clean and both valves to have been seating properly. The piston rings were in good condition and free in the grooves. There was little carbon in any of the grooves. The piston crown was coated

with an adherent layer of carbon; 0 002 in. thick at the center, shading to black at the periphery and increasing in thickness to about 0.005 in.

The coating on the inlet valve was similar to that on the piston crown. There was a reddish coating about 0.005 in. thick on the exhaust valve and a similar coating on the water cooled surfaces. The color is attributed to iron oxide derived from additions of iron carbonyl to fuel S.

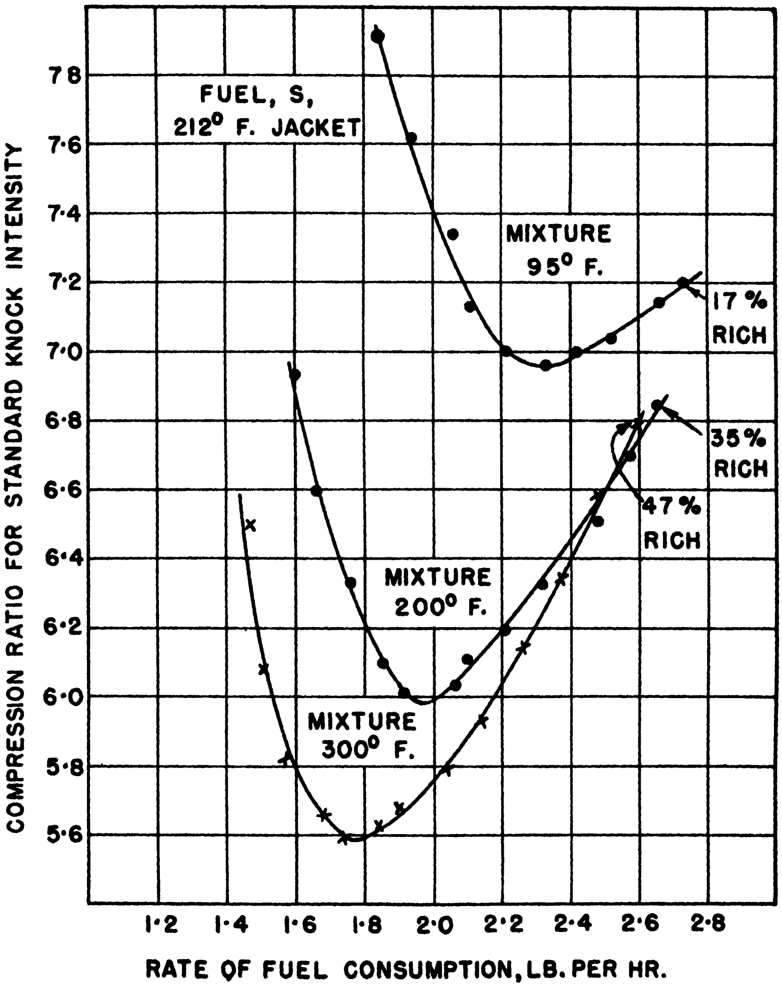

FIG. 4. *Fuel S, Lot 1. 212° F. jacket temperature.*

Standard intensity of knock was determined for rates of fuel consumption varying by steps over the range possible in the flow control conditions already described, with the mixture unheated, and at temperatures of 200° and 300°F. and with jacket temperatures of 150° and 212°F. The experimental results are given by the graphs of Figs. 3, 4, 5, and 6. It will be noted that the rate

of fuel consumption required for the critical mixture strength decreases with increase in mixture temperature as would be expected in view of the consequent decrease in the *weight* of air aspirated per stroke.

Experiments with Fuel S

The fuel contains volatile fractions in some proportion to provide for ease of motor car engine starting, but the graph of Fig 1 shows that 35% only boils at temperatures below 200°F. and 74% at temperatures below 300°F. The corresponding vapor pressures and the depression in the carburetor throat determine the maximum rate of fuel consumption when the float chamber is in

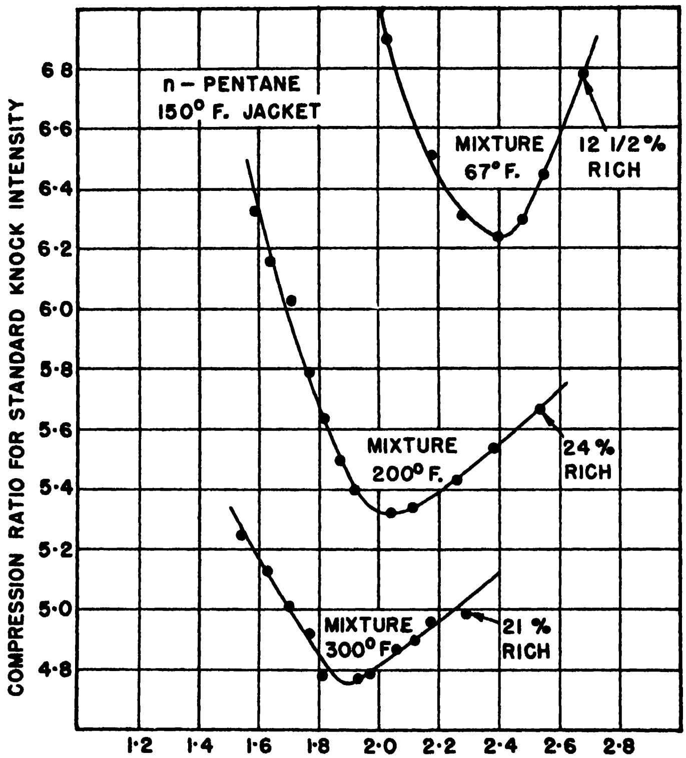

FIG. 5. *n-Pentane 150°F. jacket temperature.*

the "up" position. The maximum rate possible with a particular diameter of flow control orifice therefore diminishes with increasing mixture temperature. Thus, referring to experiments at 150°F. jacket temperature, Fig. 3, the maximum rate of fuel consumption diminished from 2.89 to 2.56 lb. per hour as mixture temperature was increased from 78° to 300°F. In the same circumstances the rate of fuel consumption required to maintain the critical mixture strength, at which the minimum compression ratio giving standard knock intensity occurs, diminished from 2.50 to 1.90 lb. per hr. The maximum

mixture strengths obtainable varied accordingly as shown by the percentages given on the graphs.

Experiments with n-Pentane (Figs. 5 and 6)

Pentane was selected as the second fuel because of the expectation that the mixture heating means available would suffice for complete vaporization prior to admission to the engine cylinder. The experiments were made during hot summer weather and there was generally a tendency to form vapor in the fuel

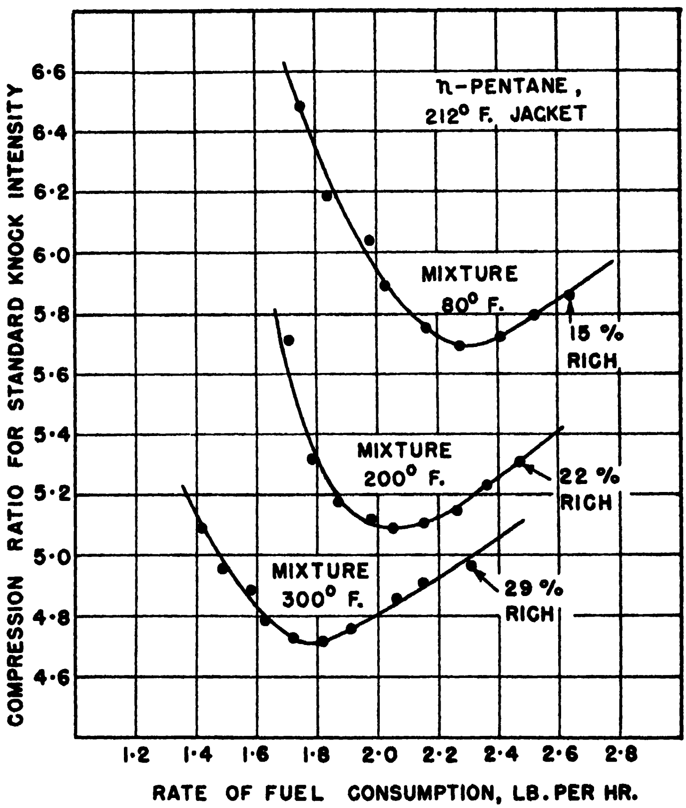

FIG. 6. *n-Pentane. 212° F. jacket temperature.*

line to the carburetor. On one occasion when the official Toronto shade temperature was 101°F., the pentane boiled in the float chamber and the experiment could not be continued.

The relatively high vapor pressure of the pentane assisted vaporization but placed a relatively low value on the maximum possible rate of consumption because of the lower than atmospheric pressure in the carburetor throat. Thus at 212°F. jacket temperature and 300°F. mixture temperature, Fig. 6, the maximum rate of pentane flow was 2.30 lb. per hr. whereas when using the less volatile fuel S the maximum flow was 2.60 lb. per hr. The degrees of

enrichment obtained in the conditions of the experiments are shown on the graphs of Figs. 5 and 6 and suffice for the purpose of the investigation.

Experiments with Fuel S Doped with Iron Carbonyl

The experiments were carried out with the cylinder jacket at 212°F. and the mixture at 300°F. The fuel was from a lot of 50 gal. of old stock and differed

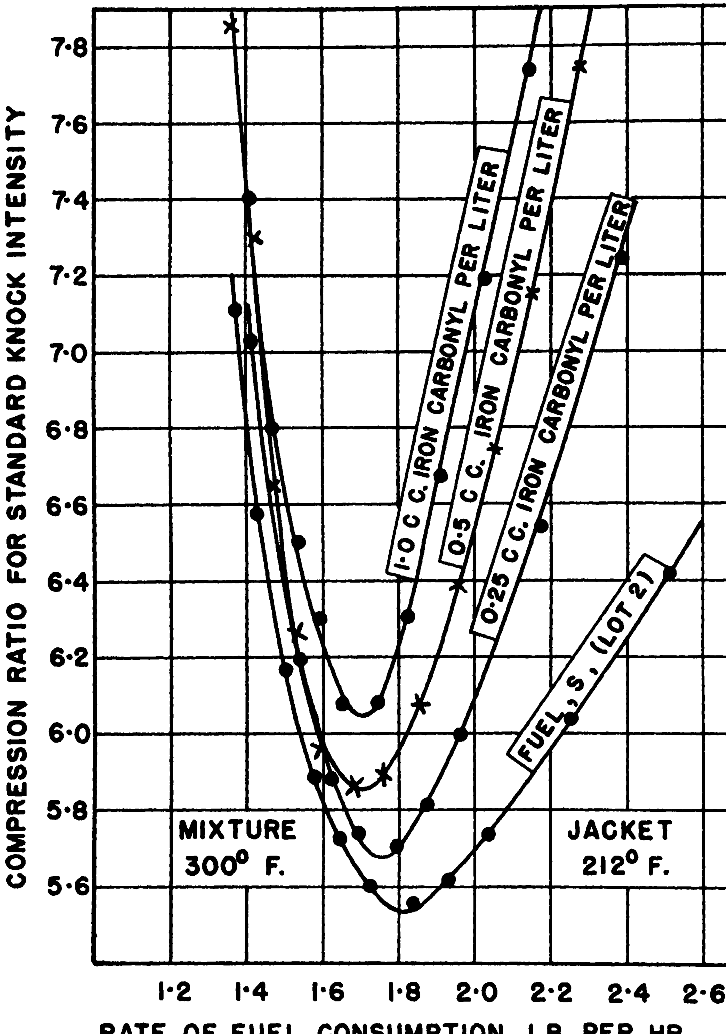

FIG. 7. *Fuel S, Lot 2, and with iron carbonyl in concentrations increasing to 1.0 cc. per liter.*

slightly in antiknock value and considerably in "mixture response" from that used previously which was obtained as required from a local service station.

The influence of enriching the mixture on the antiknock effect of iron carbonyl is shown by the graphs of Fig. 7. The increase in the antiknock

effect obtained on increasing mixture strength is quite remarkable. Thus the compression ratio for standard intensity of knock when using the undoped fuel at the critical mixture strength is 5.54, rate of fuel consumption being 1.8 lb. per hr. but on increasing the rate to 2.2 lb. per hr. and adding iron carbonyl in the concentration of 1.0 cc. per liter, that is, one-tenth of one per cent, the compression ratio for standard intensity of knock rose nearly 2.5 compression ratios, to 8.0:1.

Generally similar results were obtained when the fuel was doped with tetraethyl lead or nickel carbonyl. Those for iron carbonyl are presently given because the substance was used in experiments described in Part VII (7), showing that enriching the mixture increases the oxidation promoting effect of the antiknock.

Discussion of the Experimental Results

It was shown by oxidations in reaction chamber No. 10, described in Part VII (7), that over the temperature range 600° to 650°C. reaction velocity increased by 100% on enriching a pentane-air mixture from 25% weak to 100% rich. The reaction products at the high temperatures were steam and the oxides of carbon. Reaction velocity was greatly accelerated by iron carbonyl, the temperature of any particular rate of reaction being reduced by as much as 150°C., and the reaction products were steam and carbon dioxide only. The high temperature oxidation products are all antiknocks and if present in the end gas of an engine would reduce the tendency to detonation or knocking combustion as discussed in Part III (6).

The antiknock property of *rich mixtures* is indicated by the slope of the graphs for mixture strengths greater than the critical value, that is, by the ratio,

$$\frac{\text{Increase of compression ratio for standard knock intensity}}{\text{Increase in rate of fuel consumption}}.$$

The ratio will be designated by the letter, R. The experimental results summarized accordingly are given in Tables I, II, and III.

Pentane Boiling Range 95° to 97.4°F. (Table I)

The jacket temperature being 150° and the mixture temperature 67°F., $R = 2.4$; then on heating the mixture to 200°F., more of it is vaporized prior to entering the cylinder; the cooling effect diminishes accordingly and R decreases to 0.86. A further increase of mixture temperature to 300°F. reduces R to 0.70, indicating that the cooling effect has been reduced but not eliminated.

The results for a jacket temperature of 212°F. can now be considered. Starting with a mixture temperature of 80°F., the value of R is 0.70 only. It diminishes to 0.56 when the mixture is heated to 200°F. and remains un-

changed, within the accuracy possible, on further heating the mixture to 300°F. The conclusion is that the pentane was vaporized completely when the mixture temperature was raised to 200°F. and that the value of R then obtained represents the antiknock effect arising from the increase in rate of oxidation due to increasing the mixture strength by 29%.

TABLE I

EXPERIMENTAL RESULTS—PENTANE

Jacket temp., °F.	Mixture temp., °F.	Ratio R	Jacket temp., °F.	Mixture temp., °F.	Ratio R
150	67	2 4	212	80	0.70
150	200	0 86	212	200	0 56
150	300	0 70	212	300	0 54

Fuel S, Lot 1, Boiling Range 85° to 430°F. (Table II)

The jacket temperature being 150°F. and the mixture temperature 78°F., vaporization would occur mainly in the cylinder, the maximum cooling effect would be obtained, and $R = 1.7$. The large increase of mixture temperature to 200°F. reduces R to 1.6 only and on further increasing mixture temperature to 300°F., R *increases* to 2.1. Thus, as the proportion of the fuel vaporized

TABLE II

EXPERIMENTAL RESULTS—FUEL S (LOT 1)

Jacket temp., °F.	Mixture temp., °F.	Ratio R	Jacket temp., °F.	Mixture temp., °F.	Ratio R
150	78	1 7	212	95	0 6
150	200	1 6	212	200	1 6
150	300	2 1	212	300	2.5

outside the cylinder increases and the cooling effect diminishes accordingly, R increases. This characteristic is more pronounced when the jacket temperature is raised to 212°F. and the initial mixture temperature is 95°F. R is then 0.6, increases to 1.6, and to 2.5 as mixture temperatures are raised first to 200°F. and then to 300°F. That is, the antiknock effect of enrichment *increases* as the evaporative cooling effect diminishes. This characteristic is attributed to the relatively great susceptibility to oxidation of the higher boiling point constituents of the fuel.

Fuel S, Lot 2, Plus Iron Carbonyl (Table III)

The experiments were made at jacket and mixture temperatures of 212° and 300°F. respectively. The high value of R due to the susceptibility to oxidation of the heavier fractions of the fuel is then increased by the oxidation promoting effect of the metallic antiknock. The value of R increases accordingly from

1.4 for the undoped fuel to 4.4 for a dope concentration of 0.50 cc. of iron carbonyl per liter. Little further increase of R is obtained on doubling the dope concentration. This would be expected from the experimental results described in Part VII showing that the oxidation promoting effect of iron carbonyl reaches a limiting value as concentration and mixture strength are increased.

TABLE III

EXPERIMENTAL RESULTS—FUEL S (LOT 2) PLUS IRON CARBONYL, JACKET TEMPERATURE 212°F., MIXTURE TEMPERATURE 300°F.

Fuel	Ratio R
Fuel S undoped	1 4
Fuel S plus 0 25 cc. I.C. per liter	3 0
Fuel S plus 0 50 cc. I.C. per liter	4 4
Fuel S plus 1 00 cc. I.C. per liter	4 5

Conclusions

The experimental results are not in accordance with the current theory that knock or detonation in an engine is the result of an oxidation reaction in the end gas proceeding by a chain mechanism (1, 5). On the contrary, they support the view that knocking combustion tends to be prevented by dilution of the end gas with the antiknock products of the oxidation reaction occurring at the high temperature of the end gas (6), and it is concluded accordingly that:

(1) Enrichment of the fuel–air mixture used in an engine leads to an antiknock effect *in addition* to that due to the increased cooling, because of the consequent increase in the rate of oxidation of the end gas.

(2) The additional antiknock effect increases with increase in the susceptibility of the fuel to oxidation.

(3) The antiknock effect of iron carbonyl increases with increase of mixture strength because of the corresponding increase in the oxidation *promoting* effect of the substance, at end gas temperatures.

Acknowledgments

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given by Prof. George F Wright of the Department of Chemistry, University of Toronto, and by Mr. H. Shanfield of the Fuel and Oil Laboratory, National Research Council.

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SOME FACTORS AFFECTING THE CYANOGENETIC CONTENT OF FLAX[1]

By G. R. PATERSON[2] AND E. Y. SPENCER[3]

Abstract

Many factors, both inherent and environmental, affect the linamarin content of flax (its cyanogenetic principle) Redwing variety contains considerably more potential cyanide than does Royal. Flax, maintained at a high moisture level throughout the growth season, contains significantly less linamarin than that grown with access to less soil moisture. Frost, mechanical injury, and drought all affect the cyanogenetic content of flax adversely, the effect of the first being very great. Flax grown at the higher moisture level was more affected by these conditions than was flax grown at the lower moisture level. The recovery of cyanide from the glycoside by simultaneous enzymatic hydrolysis and aeration, and its estimation by the alkaline silver nitrate method, is an effective laboratory means of assessing the cyanogenetic content of flax. Although acetone, one of the decomposition products of linamarin, normally reacts with the alkaline picrate reagent, picrate under certain conditions may be adapted to the roughly quantitative estimation of cyanide by test paper in the field.

Introduction

Robinson (12), Auld (2), and Henry and Auld (8) have reviewed the history of cyanogenesis in a very comprehensive manner, one (8) with special reference to linseed. Although cyanogenesis, the occurrence of hydrocyanic acid in the plant kingdom, was discovered in 1803, it was not until 1883 that flax was found by Jorissen to be cyanogenetic. In 1891, Jorissen and Hairs isolated the cyanogenetic glycoside, linamarin, and described its enzymatic hydrolysis to hydrogen cyanide, D-glucose, and a volatile ketone giving the iodoform reaction. Dunstan and Henry showed the aglycone was acetone cyanhydrin in 1903. Linamarin is accompanied in flax (in different cells) by a specific β-glycosidase, linamarase, which hydrolyzes it to its components, hydrogen cyanide, D-glucose, and acetone. In flax, the quantity of linamarase present usually parallels the content of linamarin.

Cyanogenesis is inheritable (3), the cyanogenetic character being governed by the interaction of genes determining the presence or absence of the glycoside and the enzyme. However, the amount of glycoside present in a cyanogenetic plant is subject to variation by many other factors. Any factor which changes the normal season of growth, e.g., drought, injury (such as in a hail storm), frost, or insect attack, increases the amount of potential cyanide (4, 6, 9, 11). Many forage plants are cyanogenetic and so constitute a possible threat to the stock who feed upon them. The toxic dose for most animals is the quantity of cyanogenetic glycoside equal to about 2 mgm. of hydrogen cyanide per pound

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[2] *Holder of Research Fellowship from the Canadian Foundation for the Advancement of Pharmacy at the University of Saskatchewan. Present address: Ontario College of Pharmacy, Toronto 2, Ont.*
[3] *Associate Professor of Chemistry.*

of body weight (13). Based on the average cyanogenetic content of flax (25 mgm. % of hydrogen cyanide), a portion of less than 2 lb. would prove fatal to an animal weighing 100 lb., assuming complete hydrolysis of the glycoside. Under abnormal conditions of growth (frost especially), flax may contain two to three times as much potential cyanide and so constitute a serious menace to stock. However, many substances have an inhibiting effect on the release of hydrocyanic acid from linseed cake (2, 8), among them glucose, salt, and the crude fiber of certain green fodders. It is recommended that these be fed along with linseed cake or other cyanogenetic plants. The use of the defatted residue, after hot-press oil extraction of flax, should be encouraged, since it contains little active enzyme owing to its destruction at the temperature employed (8).

Methods and Materials

A greenhouse experiment was designed to assess the effect of various climatic factors as well as varietal effect on the cyanogenetic content of flax (10). Two varieties of flax were chosen –Royal and Redwing. The wilting level and moisture capacity of a soil mixture of seven parts of top soil, two parts of sand, and one of manure (subsequently used as the growth medium in the experiment) were determined as 15.5% and 28% respectively. It was decided therefore to grow both varieties at soil moisture levels of 18% and 27%, termed hereafter "low moisture" and "high moisture" levels. Each variety at each moisture level was submitted to four conditions, control, frost, injury, and drought, making a total of 16 treatments. Each treatment consisted of six pots containing an average of nine plants each.

Moisture levels were maintained by weekly watering, distribution of the water evenly in the soil mixture being aided by means of a sand column. The conditions of frost, drought, and injury were attained or simulated in the following manner. A month after first flowering, the plants which were to be frosted were placed in a separate section of the greenhouse, where, over the course of four days, the temperature was gradually lowered to 32°F. On the evening of the fourth day, the temperature was allowed to fall still lower, reaching a minimum of 24.5°F. The plants were allowed to proceed towards maturity, having been submitted, after a hardening process, to freezing temperatures for four to five hours. In the drought experiments, 10 weeks after planting, the plants were withdrawn from their normal weekly watering schedules, which were not resumed until the plants had reached the wilting levels. The procedure was repeated before the plants were allowed to go on towards maturity with the regular moisture levels. A week to ten days after flowering, each plant in the 24 "injury" pots was pinched twice at the base of each stem supporting a flower, with a self-closing clothespin. This procedure corresponded to that used by Franzke and Hume (6) in their experiments on Sorghum, and was intended to simulate mechanical injury such as might result in many ways during the growing season, and during harvesting.

At maturity the seeds were collected and cleaned. Just before the cyanide determinations were carried out, the seeds were ground in a glass mortar. Where possible, two assays were made on the yield from each pot. To the ground sample, in the tube of a Van Slyke – Cullen Aeration Apparatus (7), was added a trace of granular stearic acid to prevent frothing, and 10 ml. of distilled water. After 15 min. maceration (the sample tube of the apparatus being suspended in a thermostat maintained at 45°C.), air was passed through the mixture at a slow steady rate for two hours. The 45° temperature maintained was the optimum temperature for enzymatic hydrolysis of the cyanogenetic glycoside linamarin to its decomposition products, D-glucose, acetone, and hydrogen cyanide. An alkaline trap (10 ml. of $N/10$ aqueous sodium hydroxide) completely removed the hydrogen cyanide from the air circulated through the sample. Five milliliters of concentrated ammonium hydroxide and 2 ml. of 5% aqueous potassium iodide were added to the contents of the trap, and the estimation of the cyanide was carried out with $N/800$ aqueous silver nitrate, according to the method of Liebig, as modified by Sharwood (14).

Attempts were made to find a test paper suitable for the roughly quantitative estimation of potential cyanide in flax. Among the tests tried were the copper acetate – benzidine acetate (5), the copper sulphate – guaiacum (5), the phenolphthalin (15) and the alkaline picrate method (1), the last-named despite the fact that acetone, a decomposition product of linamarin, normally reacts with the reagent (10). In each case, a small piece (5 by 60 mm.) of filter paper, impregnated with the specific reagent, was suspended in a corked 10 by 75 mm. test tube above 0.025 to 0.100 gm. of finely ground flax, moistened with distilled water and left at room temperature.

Results and Discussion

The results obtained from the analyses of the samples are listed in Table I

TABLE I

MEAN HYDROGEN CYANIDE CONTENT OF ROYAL AND REDWING FLAX FOR EIGHT TREATMENTS

Moisture level	Condition	Royal		Redwing	
		No. of samples	Mean mgm. % HCN	No. of samples	Mean mgm. % HCN
Low	Control	11	26 4	11	33 7
Low	Frost	4	47 2	11	57 9
Low	Injury	11	29 0	11	34 7
Low	Drought	8	26 7	9	36 1
High	Control	11	19 6	12	23 0
High	Frost	7	47 7	12	49 6
High	Injury	10	24 5	11	26 8
High	Drought	9	26 8	11	28.1
		71	28 9	88	36 2

Of the 192 theoretically possible samples, 33 (17.2%) were lost owing to (*a*) plant fatality due to frost or injury, (*b*) poor yield due to adverse effects created by the various treatments, and (*c*) laboratory accidents. The average cyanogenetic content of the 159 samples was 32.9 mgm. % of hydrogen cyanide. Table I illustrates that in all comparable treatments Redwing contains more potential cyanide than Royal. Table III shows that this constant difference is highly significant.

The usual method of analysis of variance could not be carried out for these data owing to the irregularity of numbers of samples for the different treatments. Therefore, the Yates' method of unweighted means for the disproportionate subclass numbers (assuming interaction present) was used for the present analysis (16). The analysis of variance is shown in Table II. *F* values show that the effects of variety and of soil moisture level are highly significant.

TABLE II

ANALYSIS OF VARIANCE TO DETERMINE EFFECT OF VARIETY, MOISTURE, FROST, INJURY, AND DROUGHT ON CYANOGENETIC CONTENT OF FLAX

Sources of variation due to	*F*
Varieties	412 41**
Moisture	247 12**
Treatments	934 18**
$V \times M$	96 66**
$V \times T$	1 13
$M \times T$	6 84**
$V \times M \times T$	43 90**

** *Significant beyond the 1% point.*

The total effect of the treatments is also very great. The secondary interactions, in two of three cases, are highly significant. The soil moisture level has a differential effect on the two varieties as well as on the conditions imposed. However, variety does not in any way alter the effect of the treatments applied. The tertiary interaction is highly significant, doubtless owing to the two significant secondary interactions.

Table III is introduced to illustrate the effect of the individual conditions, as well as to confirm the significance of variety and moisture. Flax grown in soil of lower moisture content contains significantly more linamarin than flax grown with access to more soil moisture. Redwing flax contains significantly more potential cyanide than does Royal. While frost more than doubles the amount of cyanogenetic glycoside in flax, injury and drought merely increase

TABLE III

SUMMARY OF EFFECTS OF VARIETY, MOISTURE, AND CONDITION (FROST, INJURY, DROUGHT) ON THE CYANOGENETIC CONTENT OF FLAX

Classification	Mean, mgm % HCN	$d \pm S.E._d$
Moisture		
Low moisture	35.9	5.6 ± 0.35**
High moisture	30.3	
Variety		
Royal	28.9	
Redwing	36.2	7.3 ± 0.36**
Condition		
Control	25.6	
Frost	51.6	26.0 ± 0.51**
Injury	28.8	3.2 ± 0.48**
Drought	29.4	3.8 ± 0.49**

** Significant beyond the 1% point

the quantity by an average of 13% and 17% respectively. However, the action of all three climatic factors is significant at the 1% level, as shown in Table III. Fig 1 illustrates all these effects graphically.

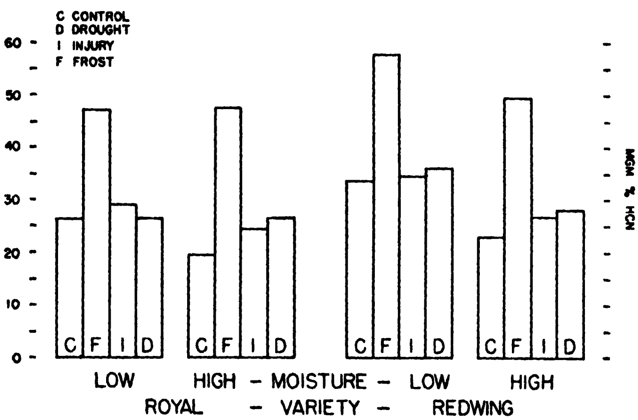

FIG 1 *Effect of some factors on hydrogen cyanide content of flax.*

Acetone normally reacts with the alkaline picrate reagent in the same way as hydrogen cyanide. A positive test for acetone in the alkaline trap was obtained by means of the iodoform reaction. However, $M/50$ and $M/100$ aqueous solutions of acetone had little or no effect on alkaline picrate paper suspended above them for 24 hr. Under similar conditions, $M/50$ and $M/100$ solutions of hydrogen cyanide, and a solution $M/100$ with respect to both, reacted almost immediately with the reagent, reaching maximum intensity of color in 20 to 30 min. The last (with acetone added) showed no deeper color than did

its control. On the other hand, test paper suspended above ground flax moistened with water and containing 0.031% hydrogen cyanide did not begin to change color for 90 min. and reached maximum color in six to eight hours. This delay in color formation was doubtless due to slow hydrolysis at room temperature. It seems likely that alkaline picrate test paper may be used for the preliminary estimation of potential cyanide in flax. The test appears able to detect differences of about 10 mgm. %.

Acknowledgments

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LIQUID AND FROZEN EGG

V. VISCOSITY, BAKING QUALITY, AND OTHER MEASUREMENTS ON FROZEN EGG PRODUCTS[1]

BY JESSE A. PEARCE[2] AND C. G. LAVERS[3]

Abstract

Freezing irreversibly increased the viscosity of yolk and whole egg, but did not affect the white. Vigorous mechanical treatment before freezing reduced the viscosity of defrosted yolk, white, and whole egg. The viscosity of defrosted yolk and whole egg increased with increase in freezing or thawing time. Mechanical pretreatment or differences in freezing time did not affect the baking quality of defrosted egg products. Freezing reduced the baking quality of yolk and whole egg, but the baking quality improved after storage for about three months at − 10° and 0° F., and then decreased. A thawing time of four hours resulted in yolk or whole egg of better baking quality than thawing times of 0.03, 24, or 48 hr. There was no relation between viscosity and the baking quality of these egg products. The addition of 2% sodium chloride was equivalent to the addition of 8% sucrose in preserving the foaming quality of frozen yolk.

Introduction

Previous papers in this series have been concerned primarily with the development of tests for measuring eating quality and for determining the solids content of frozen egg. Since frozen egg is used chiefly by the baking trade, it was believed desirable to assess the effects of prefreezing treatment, freezing time, storage time, and thawing time on the baking quality of defrosted egg products. This paper describes the effect of all these factors on baking quality, as assessed by measurements of baking volume or foaming volume (7); and the effect of some of them on other measures, such as viscosity (9), fluorescence value (6), and amino nitrogen (11).

Materials and Methods

Fresh Grade *A* large eggs were used to prepare the experimental materials, which, unless otherwise stated, were mixed for five minutes in a "Mixmaster" at No. 10 speed, strained through cheese cloth to remove particles of shell and chalaza, poured into Reynold's metal A-10 bags with a capacity of about

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[2] *Biochemist, Food Investigations.*

[3] *Formerly Chemical Engineer, Food Investigations; present address, Research Department, Maple Leaf Milling Co., Toronto.*

one liter (3 by 4 by 5 in.), and frozen in about 10 hr. Freezing was considered complete when a thermocouple in the center of the block of egg reached 20° F. at which point approximately 6% of the water remains unfrozen (8). The time for the liquid to pass from about 45° to 20° F. was recorded as the freezing time.

Defrosting was done in about 15 hr., unless otherwise stated. Defrosting time was defined as the time for the liquid to pass from a temperature of 0° F. to about 35° to 40° F. After defrosting and before testing, the liquid was again mixed at a temperature of 50° F. in a "Mixmaster" for one minute at No. 1 speed. White and whole egg usually became reasonably homogeneous after this mixing period, but as mixing did not make the more viscous samples of yolk homogeneous, their viscosity was tested in the heterogeneous state.

Many of the tests were those used in previous studies in this series (4), and included measurements of pH, reducing sugar, viable bacterial count, volume measurements on test sponge cakes, and foaming volume measurements. Baking and foaming volume measurements were made on defrosted white mixed with freshly separated yolk and on defrosted yolk mixed with freshly separated white. These mixtures were equivalent in composition to freshly broken whole egg. For these baking quality tests, the most viscous yolk could be mixed with egg white, but it was more difficult to use than yolk of low viscosity.

Fluorescence was measured on a serum extracted from whole egg (6), and amino nitrogen was determined in whole egg and in yolk by Van Slyke's method (11). Viscosity was measured on defrosted egg liquids at 50° F. with a Gardner-Parks mobilometer (9), which consists of a cylinder to contain the liquid under study, and a piston that is allowed to fall a measured distance through the liquid. The pistonhead can be changed to provide more or less resistance and the weight on the piston can be varied. The 51-hole disk (pistonhead) was used with a total weight of 100 gm. including the piston for defrosted white, or whole egg, and with a total weight of 1600 gm. for defrosted yolk. The time in seconds for the piston to fall 20 cm. was taken as a measure of viscosity.

Effect of Prefreezing Treatment on Quality

Mechanical treatment of whole egg before freezing was believed to retard the gelation that occurs during frozen storage (9). This phase of the study was designed to examine the effect of mechanical treatment of whole egg, yolk, and white on viscosity, baking quality, and pH of the stored, frozen product. Strained liquid was treated in four ways: no further treatment, 15 min. additional mixing, dispersion in a laboratory hand homogenizer, and dispersion in a colloid mill. All mixing and dispersing was done in a manner that minimized the introduction of air and the resulting foam. The products were stored at −10° F.

The various mechanical treatments did not affect the baking volume, foaming volume, or pH of whole egg, yolk, or white, whether measured before freezing, after freezing or after frozen storage.

Table I shows that increasing the severity of the mechanical treatment reduced the mobilometer readings, i e., the viscosity, of unfrozen and defrosted whole egg, yolk, and white. Average readings are given in the table because none of the materials showed any change in viscosity during storage for three

TABLE I

EFFECT OF MECHANICAL TREATMENT ON THE VISCOSITY OF UNFROZEN AND DEFROSTED EGG PRODUCTS

Treatment	Mobilometer reading, sec.	
	Before freezing	After freezing*
Whole egg		
Mixed		
Mix. 5 min	3.2	178
Mix 20 min	2.4	151
Dispersed		
Mix 5 min + homogenizer	1.5	10
Mix 5 min + colloid mill	1.3	10
Yolk (1600 gm weight on piston when used on defrosted yolk)		
Mixed		
Mix 5 min	27	455
Mix 20 min	26	315
Dispersed		
Mix 5 min + homogenizer	19	236
Mix 5 min + colloid mill	18	129
White		
Mixed		
Mix 5 min	6.5	4.0
Mix 20 min	2.9	2.6
Dispersed		
Mix 5 min + homogenizer	1.3	1.3
Mix 5 min + colloid mill	1.1	1.1

**Average after storage for 0, 1, 2, and 3 months at − 10° F*

months at −10° F. Freezing did not change the viscosity of egg white, regardless of the treatment. Freezing increased the viscosity of the mixed (Mixmaster only) whole egg about 60 times but only increased the viscosity of the dispersed (colloid mill or homogenizer) whole egg by about eight times. Freezing caused so great an increase in the viscosity of yolk that the weight on the piston had to be increased from 100 to 1600 gm, which interferes with comparisons of the data. Nevertheless there is evidence that dispersed yolk changes less in viscosity during freezing than the mixed yolk.

Effect of Freezing Time on Quality

The liquid was frozen at different temperatures and with different thicknesses of insulation around the Reynold's metal containers, to provide different freezing rates. The bacterial count in the initial, laboratory-prepared material was only about 50 per ml. A count of the same order was observed in products frozen in less than 12 hr., but the count increased to 300 per ml. in product frozen in about 24 hr. and to 1000 per ml. in product frozen in 100 hr. High bacterial counts are usually observed in the cores of commercially prepared cans of egg that have been frozen too slowly. However, after a period of frozen storage, there is usually a marked decrease in the bacterial count (2, 12).

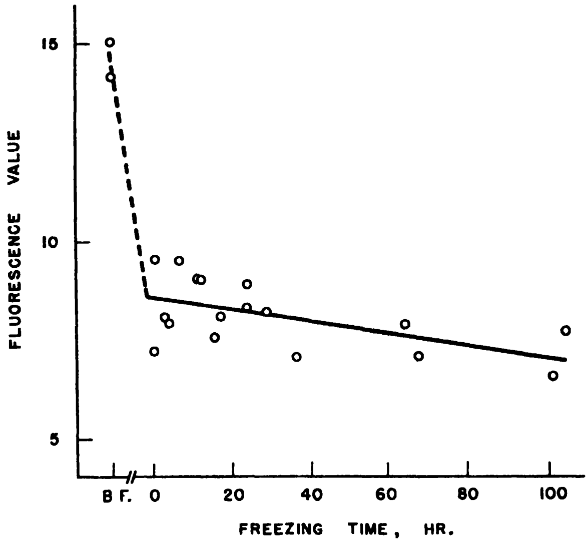

FIG. 1. *Effect of time of freezing on the fluorescence value of a serum extracted from whole egg.*

A visual examination of the effect of freezing time on color and structure showed that material frozen in 10 min. was light yellow in color. As the freezing time was increased, the color of the product deepened, and at a freezing time of 110 hr. became a dark orange. The frozen product had a laminar structure. If frozen in 10 min., the flakes were alternately opaque and transparent and about 0.001 in. thick. If frozen in 25 hr. the flakes were about 0.05 in. thick, while material frozen in 60 and 100 hr. had a granular structure to a depth of about 2 in., but the center had a laminar structure in which the transparent flakes were about 0.1 in. thick.

Freezing and the time of freezing had no effect on either the reducing sugar or the amino nitrogen content of eggs. The reducing sugar content of whole egg remained at 0.38 mgm. per 100 ml. of egg, regardless of the freezing time. The amino nitrogen content of 5-ml. samples of whole egg and of yolk was 6.90 and 9.66 mgm. respectively, whether frozen or unfrozen.

Fig. 1 shows that freezing appreciably reduced the fluorescence of a serum extracted from whole egg. Increasing the freezing time from about 10 min. to 100 hr. reduced the fluorescence of this extract still further. It is unlikely that this is due to factors other than the rate of freezing, since all measurements shown were made at the same time. These results differ from some other published information. The fluorescence of dried eggs, prepared from liquid egg frozen at different rates, increased with increase in freezing time (5); but freezing and defrosting of extracts containing these fluorescing substances caused a reduction in fluorescence (3). Prolonged storage of frozen egg caused an increase in fluorescing substances (4).

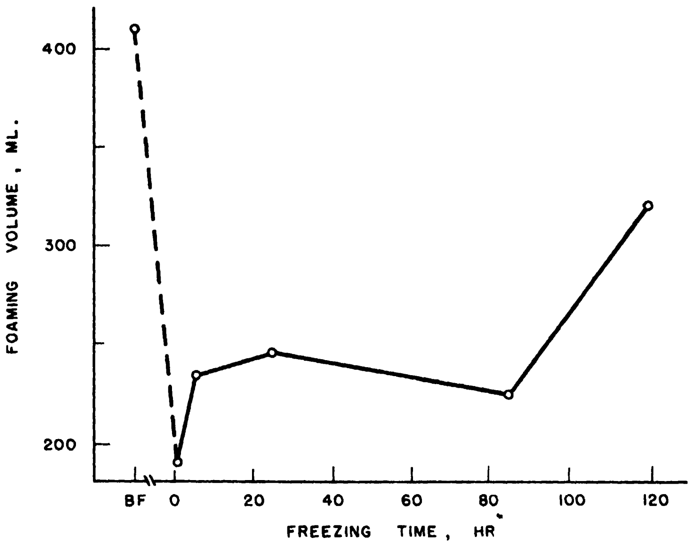

FIG. 2. *Effect of freezing time of yolk on the foaming volume of defrosted yolk mixed with unfrozen white.*

In general, freezing time had little effect on the foaming volume of defrosted whole egg or egg white, but it did affect foaming in defrosted yolk. Unfrozen whole egg had a foaming volume of about 400 ml. Frozen whole egg had a foaming volume of about 375 ml., regardless of the freezing time, while the foaming volume for mixtures of frozen white and unfrozen yolk was about 390 ml. regardless of the freezing time of the white. Fig. 2 shows that freezing yolk in about 100 hr. gave a product which, when mixed with an amount of unfrozen white to give whole egg liquid of correct proportions, had a foaming volume of about 300 ml., while yolk frozen in 10 min. had a foaming volume of only about 200 ml.

The Effect of Added Salt and Sugar on Frozen Yolk

Some explanations have been given for the effectiveness of sodium chloride and sucrose in reducing gelation in frozen yolk (1, 9). Since these substances are used commercially for this purpose (10), it was of interest to see if their

use also affected baking quality of yolk as reflected by foaming volume measurements. Therefore, 2, 4, and 8% of these compounds were added to yolk before freezing, and the samples were examined immediately after defrosting.

Fig. 3 shows that 2% sodium chloride had a marked effect in retaining the foaming volume of frozen yolk, and that increasing the amount of salt had

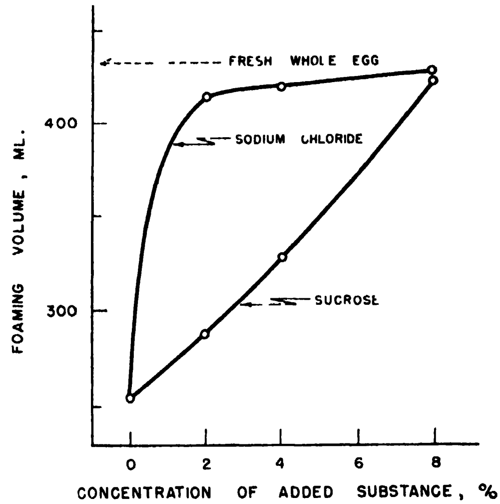

FIG. 3 *Effect of added sodium chloride and sucrose on the foaming volume of defrosted yolk and unfrozen white.*

only a slight additional effect. Increasing the amount of sucrose up to 8% had a progressively greater effect in retaining foaming volume: 8% sucrose gave a product that was about equal to fresh egg.

Effect of Storage Time on Quality

An earlier study in these laboratories indicated a decrease in the baking quality of freshly frozen whole egg (4). Therefore, it was of interest to re-

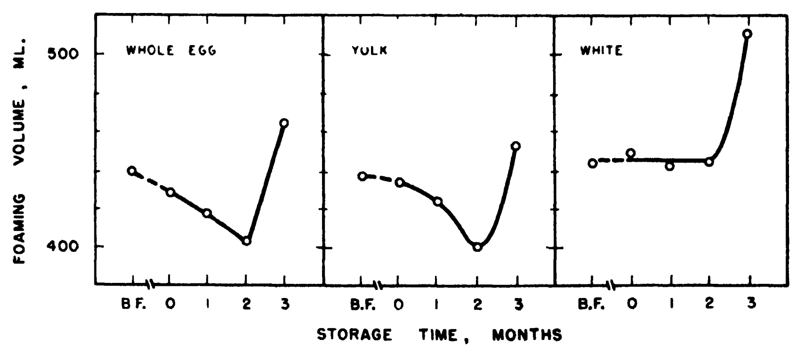

FIG. 4. *Changes in the foaming volume of stored frozen egg products: defrosted yolk mixed with unfrozen white, and defrosted white mixed with unfrozen yolk.*

examine the effect of storage up to about three months at − 10° F. on the quality of yolk, white, and whole egg.

Freezing and time of frozen storage effected measurable pH changes, in white and in whole egg, but pH could not be measured in defrosted yolk because of its high viscosity. Egg white had a pH of 9.0 before freezing, which increased to 9.1 after freezing and then gradually decreased to 8.9 at the end of three months' storage. Whole egg had a pH of 7.5 before freezing, which became 7.6 after freezing and then gradually increased to 7.8 after three months' storage. These pH changes in frozen whole egg were similar to those observed previously (4).

Fig. 4 shows that both whole egg and yolk decreased in foaming volume during freezing and the first two months of frozen storage, and then increased

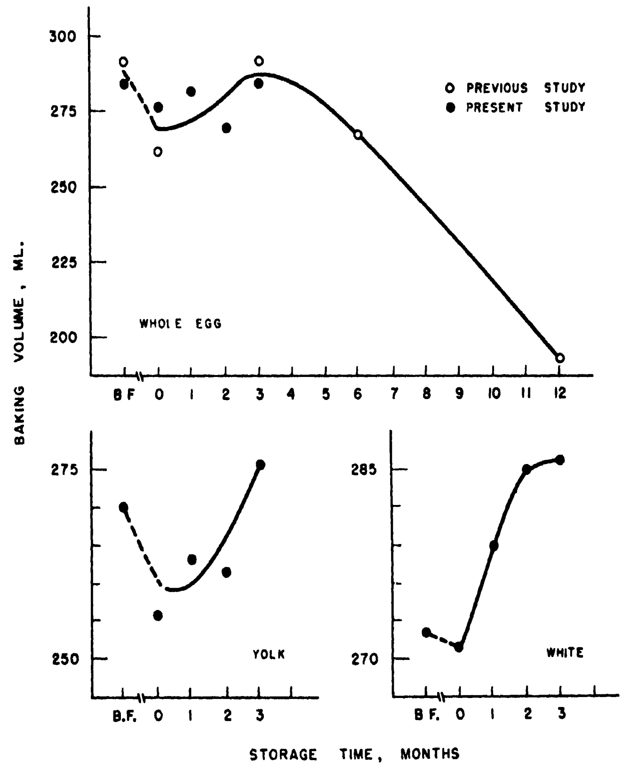

FIG 5. *Changes in the baking volume of sponge cakes made from frozen egg products: defrosted yolk mixed with unfrozen white, and defrosted white mixed with unfrozen yolk.*

in foaming volume. The foaming volume of egg white remained constant during the first two months of storage, and increased during the third month. Earlier work showed that 12 months' frozen storage appreciably reduced the foaming volume of frozen whole egg (4).

Fig. 5 shows the reduction in baking quality resulting from freezing yolk or whole egg and the subsequent increase in quality after about three months'

storage. The baking quality of egg white appeared to be unchanged by freezing but to increase during the first three months' storage. In general, foaming volume and baking volume show similar changes during frozen storage and the results presented here support previous observations on stored, frozen whole egg (4).

Effect of Freezing and Thawing Time on Quality

During the preceding phase of this study, there was some evidence that thawing time might also have some effect on quality. Therefore, a more comprehensive study was made to examine the effects of freezing time (0.2, 4, 16, and 39 hr.), thawing time (0.03, 4, 24, and 48 hr.), and storage time (0, 1, 2, 4, and 8 months) at 0° F. on viscosity and baking volume of yolk and whole egg.

Just as this study commenced, the oven used in previous baking studies broke down. With the temporary equipment used, pending receipt of a new oven, the cakes were about 30 ml. smaller than usual. Therefore, while the results for this portion of the work are comparable within themselves, they cannot be readily compared with those of previous work.

The changes in viscosity and baking volume were assessed by an analysis of variance. Each of the factors under study had a significant effect on the viscosity of defrosted yolk and whole egg, but only thawing time and storage time had a significant effect on baking quality.

Fig. 6 shows the similarity in effect of these factors on the viscosity of both yolk and whole egg, except that yolk was much more viscous than whole egg. In general, increases in freezing time from 0.2 to 39 hr. caused progressive increases in viscosity; increases in defrosting time from 0.03 to 24 hr. caused increases in viscosity, but increases in thawing time from 24 to 48 hr. caused no further increase in viscosity. Storage time caused no increase in viscosity if the product was frozen or defrosted in four hours or less, but increasing the storage time increased the viscosity in product which had been frozen or defrosted in longer times. Measurements elsewhere had indicated maximum viscosity in defrosted whole egg after two to four months' storage (9); the present results showed a progressive increase in viscosity of slowly frozen or defrosted egg throughout an eight month storage period at 0° F.

In general, while viscosity was not related to the baking volume of defrosted yolk or whole egg, material of low viscosity was more easily prepared for baking. Frozen yolk was much more viscous than frozen whole egg, and usually gave cakes about 20 ml. smaller. However, the difference in cake volume was attributable to factors other than the freezing operation, since cakes made from yolks that had been mechanically mixed, but not frozen, and added back to white also gave cakes about 20 ml. smaller than those from whole egg (Fig. 5).

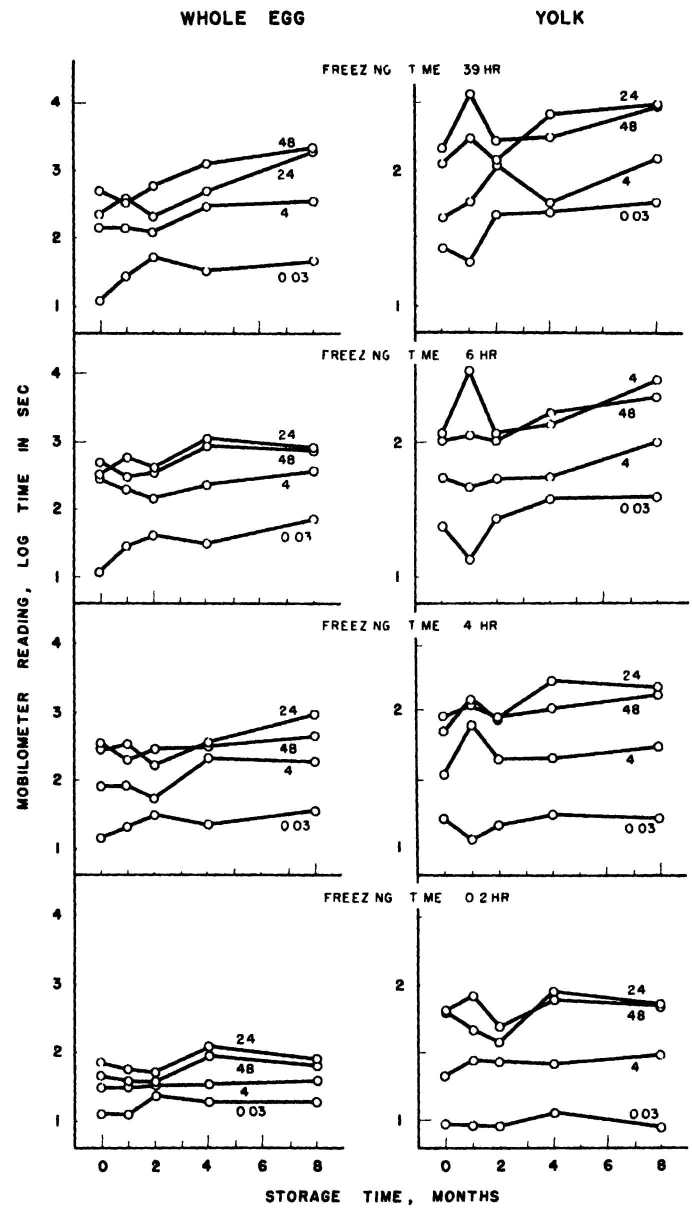

FIG. 6. *Effect of freezing time, thawing time (small labelled figures give the thawing time in hours), and storage time on the viscosity of defrosted yolk and whole egg.*

Fig. 7 shows that product thawed in four hours gave cakes with greater volume than product thawed in shorter or longer thawing times. While these differences were statistically significant, the increase in baking volume was only about 3%, which may not be of practical value in commercial processing.

Storage time had effects on the baking volume of cakes made from defrosted whole egg similar to those shown in Fig 5 The baking volume of defrosted yolk was decreased by freezing and increased after four months' storage in a manner similar to that shown in Fig 4, but in addition, there was evidence that the baking volume of defrosted yolk decreased between four and eight months' storage

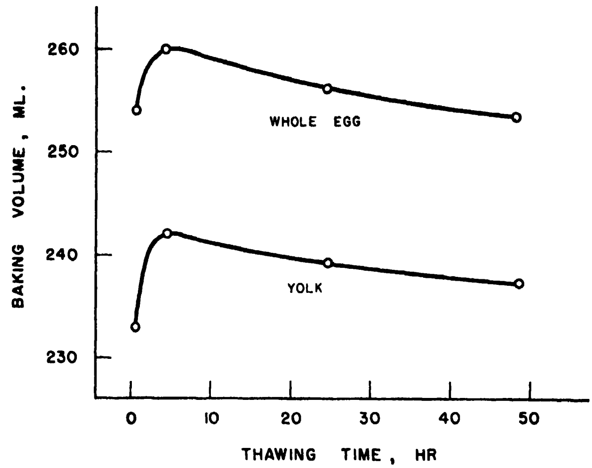

FIG 7 *Effect of thawing time on the baking volume of sponge cakes made from defrosted whole egg, and from defrosted yolk mixed with unfrozen white Values averaged over all freezing times and storage times*

Acknowledgments

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THE THIAMINE AND RIBOFLAVIN CONTENT OF MANITOBA GROWN WHEAT, OATS, AND BARLEY OF THE 1946 CROP[1]

ALLEN D. ROBINSON,[2] LANGTRY E. LYND,[3] AND BARBARA J. MILES[3]

Abstract

Some 200 samples of pure varieties of barley, oats, and wheat grown in Manitoba in 1946 were assayed for thiamine and riboflavin. Expressed as micrograms per gram the averages and ranges for thiamine were: barley 4.06 (3.3 to 4.9), oats 5.99 (4.4 to 7.9), wheat 4.28 (3.5 to 5.7); for riboflavin: barley 1.28 (0.9 to 1.9), oats 1.25 (0.8 to 1.7), wheat 1.12 (0.8 to 1.4). A varietal effect on thiamine content was noted. Plush barley contains more than O.A.C. 21, Exeter oats more than either Ajax or Vanguard, and Carlton wheat more than Regent, which in turn has a higher content than Thatcher. No varietal effects on riboflavin contents were found in any of the cereals. Neither thiamine nor riboflavin content of the cereals was determined by the soil zone in which they were grown. Significant positive correlations were found between protein and thiamine in oats and barley, protein and riboflavin in wheat, and ash and riboflavin in barley. A significant negative correlation between ash and thiamine in oats was observed.

Recently McElroy, Kastelic, and McCalla (9) have reported on the thiamine and riboflavin contents of wheat, oats, and barley grown in Alberta and the effect of type of soil on the amount of vitamin in each of these grains. This is a report of a similar investigation carried out with grains grown in Manitoba in 1946. As in the study to which reference has been made, the correlation between vitamin contents and those of other constituents was studied.

A large number of values have been reported for the thiamine contents of wheats. Some have been reported for other cereals as well. There are fewer data for riboflavin. Some of the published results are summarized in Table I. Several of these were reported originally in terms other than micrograms per gram and have been calculated by us to this basis.

The factors responsible for the varying amounts of vitamins in cereal grains have not been very well defined. A varietal effect in wheat seems to be well established. Jackson and Whiteside (7) and Whiteside and Jackson (12) found significant differences to exist between the thiamine contents of different Canadian hard red spring wheat varieties. Regent, Renown, and Reward are usually higher in thiamine than Red Bobs, Thatcher, Marquis, and Garnet. Andrews *et al.* (3) found differences in the riboflavin contents of different varieties of wheat. They listed the varieties tested, in the order of decreasing riboflavin contents, as Marquis, Pilot, Thatcher, Ceres, Renown, Rival.

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[2] *Associate Professor of Chemistry.*
[3] *Research Assistant.*

TABLE I

THIAMINE AND RIBOFLAVIN CONTENTS OF BARLEY, OATS AND WHEAT, MICROGRAMS PER GRAM

Reference	Thiamine		Riboflavin	
	Range	Average	Range	Average
Barley				
Andrews, Boyd, and Terry (3)	—	—	1.05–1.50	1.21
Davis, Laufer and Saletan (4)	4.91–6.52		0.78–1.14	—
Hochberg, Melnick and Oser (6)	—	3.50	—	—
McElroy, Kastelic, and McCalla (9)	—	4.60	—	1.25
Nordgren and Andrews (10)	5.68–7.33	6.49	—	—
Schultz, Atkin, and Frey (11)	3.8–9.2	6.2	—	—
Oats				
Andrews *et al.* (3)			1.10–1.45	1.30
McElroy *et al.* (9)		5.58	—	1.27
Nordgren and Andrews (10)	8.10–10.78	9.24	—	-
Schultz *et al.* (11)	4.8–10.3	7.2	—	—
Wheat				
Andrews *et al.* (3)	—		1.06–1.32	—
Davis *et al.* (4)		—	0.71–1.12	-
Johannson and Rich (8)				
Literature review	1.62–10.2	—	—	—
Original data	2.2–8.0	3.93	—	
McElroy *et al.* (9)		4.40	—	1.34
Whitney, Herren, and Westerman (13)	—	—	1.00–1.69	

Nordgren and Andrews (10) and Whiteside and Jackson (12) found environment to be a significant factor in determining the thiamine content of wheat. Wheat was grown in different localities for several seasons. Certain localities produced wheat with a higher thiamine content than others, even though the amounts varied from season to season. The features of environment that might be causing this effect were not investigated. Johannson and Rich (8), working with commercial samples of wheat, did not observe any relation between soil type and thiamine content of the grain. McElroy *et al.* (9) found the thiamine contents of wheat, oats, and barley grown on brown soils to be significantly higher than those grown on gray ones. The mean riboflavin contents of samples of wheat, barley, and oats grown on gray soils were slightly lower than those of samples grown on black or brown ones. Andrews *et al.* (3) found that the riboflavin content of wheat is not significantly affected by environment.

Some studies have been made to determine whether vitamin content is related to the content of any other constituent. Nordgren and Andrews (10) found a significant correlation between ash and thiamine in American-grown spring wheats, but not in winter or Western Canadian spring wheats. They did not find a significant correlation between protein and thiamine contents. McElroy *et al.* (9) found a positive correlation between protein and thiamine content for wheat and oats, but not for barley. No significant correlation

between protein and riboflavin was found in any of the three cereals. Johannson and Rich (8) failed to find any relation between amounts of thiamine in wheat and either protein or ash content. Whiteside and Jackson (12) after studying the distribution of thiamine in the wheat kernel conclude that the physical features of the kernel that are associated with high protein would also be associated with high thiamine. No relation has been established however which would permit the prediction of vitamin contents from those of any other constituent.

Further studies of vitamin contents of grains should yield results of interest. The effect of soil deserves more extended investigation. While some attempts have been made to determine if there is any relation between vitamin contents and the contents of other constituents, different investigators have reported different findings. The coarse grains have not been studied to the degree their importance warrants. The investigation reported herein details a study of the thiamine and riboflavin contents of barley, oat, and wheat varieties grown commonly in Manitoba. The samples were from the 1946 crop. They were assayed for protein, ash, thiamine, and riboflavin. An attempt was made to correlate these results with each other and with variety and soil zone.

Experimental

More than 200 samples of pure varieties of barley, oats, and wheat were collected. These were grown in several different parts of the province. The soil type was determined for each of these locations.

Moisture was determined on each sample by the 130° C. oven method, ash by direct ignition in the muffle furnace, and protein by the Kjeldahl procedure. Thiamine was determined by the Hennessy (5) method using an external standard and calculating results on the basis of a 94% recovery. Riboflavin was determined by the method of Andrews (1, 2) with the following modifications: an external standard was used instead of an internal one, and a solution of sodium hydrosulphite and sodium bicarbonate replaced solid sodium hydrosulphite. The results of analyses were calculated to a 13.5% moisture level.

Results and Discussion

The thiamine and riboflavin results for barley, oats, and wheat, grouped according to variety and soil type, are found in Tables II, III, and IV, respectively.

Barley

An examination of the data for barley reported in Table II reveals several interesting features. The small number of samples of Garton, together with the large standard deviation for this variety, and the large standard deviation for Sanalta make any conclusions doubtful regarding these varieties, since their averages differ from those for O.A.C. 21 and Plush by only small amounts.

TABLE II

THIAMINE AND RIBOFLAVIN CONTENT OF BARLEY GROUPED ACCORDING TO VARIETY AND SOIL ZONE

Variety	Garton			OAC 21			Plush			Sanalta		
Soil zone	No. of samples	Vitamin, μgm./gm. Mean	S.d.	No. of samples	Vitamin, μgm./gm. Mean	S.d.	No. of samples	Vitamin, μgm./gm. Mean	S.d.	No. of samples	Vitamin, μgm./gm. Mean	S.d.
Thiamine												
Rendzina	–	–	–	2	3.95	0.05	2	4.30	0.30	–	–	–
Degraded rendzina	–				–	–	1	4.5	–	–	–	–
Black earth	2	4.00	0.40	3	3.80	0.16	5	4.14	0.08	4	4.23	0.11
Black earth–rendzina	–	–	–	–	–	–	1	4.5	–	–	–	–
Dark brown steppe–black earth transition	–		–				2	4.30	0.50	3	4.17	0.20
Northern black	–		–	3	3.77	0.20	5	4.03	0.22	3	4.07	0.18
Northern black–gray black	–	–	–	–	–	–	–	–	–	1	3.3	–
Gray black	1	5.1	–	1	4.2	–	2	4.00	0.10	–	–	–
Gray wooded–gray black	–			–	–	–	1	4.2	–	1	2.9	–
Gray wooded	1	4.2	–	1	3.6	–	1	4.6	–		–	–
All soil zones	4	4.33	0.51	10	3.84	0.21	20	4.19	0.28	12	3.98	0.50
Riboflavin												
Rendzina	–	–	–	2	1.40	0.30	2	1.40	0.50	–	–	–
Degraded rendzina			–	–		–	1	1.4	–		–	–
Black earth	2	1.40	0.10	3	1.1	0.10	5	1.26	0.10	4	1.28	0.13
Black earth–rendzina	–	–	–	–	–	–	1	1.2	–	–	–	–
Dark brown steppe–black earth transition	–	–	–				2	1.35	0.05	3	1.33	0.17
Northern black	–	–	–	3	1.40	0.14	5	1.14	0.19	3	1.30	0.08
Northern black–gray black	–	–	–	–	–	–	–			1	1.4	–
Gray black	1	1.4	–	1	1.3	–	2	1.20	0.10	–	–	–
Gray wooded–gray black			–	–	–	–	1	0.9	–	1	1.3	–
Gray wooded	1	1.6	–	1	1.6	–	1	1.5	–		–	–
All soil zones	4	1.45	0.11	10	1.33	0.22	20	1.25	0.25	12	1.31	0.13

Plush contains more thiamine than OAC 21: this is true not only for the grand averages for these varieties, but for the averages for each soil zone—except gray black—on which the two varieties were grown.

There does not seem to be any effect of soil zone on the thiamine content of barley. Where there does appear to be some order, as an apparent decreasing one of rendzina, black earth, and northern black for OAC 21, Plush, and—for the last two zones named—Sanalta, the standard deviation for each group is usually as large as the difference between the averages. This was confirmed by an analysis of variance. Since the samples were not evenly distributed between varieties and the soil zones it was not possible to use all the data. But an analysis was made for OAC 21 and Plush for the five soil zones in which both were grown, the extra values being eliminated by using

TABLE III

THIAMINE AND RIBOFLAVIN CONTENT OF OATS GROUPED ACCORDING TO VARIETY AND SOIL ZONE

Variety	Ajax			Exeter			Vanguard		
Soil Zone	No. of samples	Vitamin, μgm./gm. Mean	Vitamin, μgm./gm. S.d.	No. of samples	Vitamin, μgm./gm. Mean	Vitamin, μgm./gm. S.d.	No. of samples	Vitamin, μgm./gm. Mean	Vitamin, μgm./gm. S.d.
Thiamine									
Rendzina	3	5.10	0.45	–	–	–	3	5.83	0.81
Degraded rendzina	1	5.8	–	–	–	–	–	–	–
Black earth	10	5.87	0.36	5	6.80	0.93	7	5.40	0.67
Dark brown steppe–black earth transition	2	6.15	0.15	–	–	–	–	–	–
Northern black	4	6.38	0.40	2	7.75	0.15	4	5.60	1.26
Northern black–gray black	–	–	–	–	–	–	1	6.6	–
Gray black	–	–	–	2	6.05	0.35	1	4.9	–
Gray wooded–gray black	–	–	–	–	–	–	1	7.0	–
Gray wooded	2	5.65	0.25	–	–	–	–	–	–
All soil zones	22	5.89	0.55	9	6.84	0.92	17	5.66	0.91
Riboflavin									
Rendzina	3	1.20	0.08	–	–	–	3	1.20	0.08
Degraded rendzina	1	1.3	–	–	–	–	–	–	–
Black earth	10	1.15	0.19	5	1.24	0.21	7	1.21	0.10
Dark brown steppe-black earth transition	2	1.40	0.10	–	–	–	–	–	–
Northern black	4	1.13	0.28	2	1.30	0.00	4	1.30	0.21
Northern black-gray black	–	–	–	–	–	–	1	1.7	–
Gray black	–	–	–	2	1.25	0.05	1	1.2	–
Gray wooded-gray black	–	–	–	–	–	–	1	1.5	–
Gray wooded	2	1.60	0.20	–	–	–	–	–	–
All soil zones	22	1.22	0.24	9	1.26	0.15	17	1.28	0.31

tables of random numbers. In no case was the F value for soil zones as large as the 5% point. The difference between the thiamine contents of Plush and OAC 21 was, however, found to be significant. This confirms the observations made in the preceding paragraph.

The data for riboflavin in barley appear in the lower half of Table II. The spread between the lowest variety, Plush, and the highest, Garton, is only 0.2 μgm. per gm. while standard deviations range from 0.11 for Garton to 0.23 for Plush. No one soil zone produces consistently higher or lower

values for all varieties. Most groups differ from the average for the variety by less than the standard deviation for the group. There is then no obvious effect of either soil zone or variety on the riboflavin content of barley. This was confirmed by an analysis of variance for the same varieties and soil zones as were used in the analysis of the thiamine data. There was no significant difference between either soil zones or the varieties Plush and OAC 21. In each case the F value was less than that for the 5% point.

Oats

The thiamine contents of three varieties of oats are recorded in the upper half of Table III. Exeter shows the highest values, on the average and for each group according to soil zone. It would appear that it is the best as a source of thiamine even though the standard deviation of 0.92 is rather large. Ajax and Vanguard are much the same in thiamine content. An analysis of

TABLE IV

THIAMINE AND RIBOFLAVIN CONTENT OF WHEAT GROUPED ACCORDING TO VARIETY AND SOIL ZONE

Variety / Soil zone	Carlton: No. of samples	Carlton: Vitamin, µgm./gm., Mean	Carlton: S.d.	Regent: No. of samples	Regent: Vitamin, µgm./gm., Mean	Regent: S.d.	Renown: No. of samples	Renown: Vitamin, µgm./gm., Mean	Renown: S.d.	Thatcher: No. of samples	Thatcher: Vitamin, µgm./gm., Mean	Thatcher: S.d.
Thiamine												
Rendzina	–	–	–	1	4.8	–	–	–	–	4	4.03	0.35
Degraded rendzina	–	–	–	1	5.0	–	1	4.2	–	5	3.70	0.18
Black earth	10	5.03	0.42	30	4.27	0.34	4	4.13	0.11	7	4.06	0.28
Black earth–rendzina	–	–	–	1	4.1	–	–	–	–	–	–	–
Dark brown steppe–black earth transition	1	4.6	–	3	4.38	0.23	–	–	–	2	3.9	0.00
Northern black	–	–	–	13	4.33	0.31	–	–	–	6	3.95	0.15
Northern black–gray black	–	–	–	1	4.9	–	–	–	–	–	–	–
Gray black	–	–	–	5	4.36	0.17	–	–	–	7	4.10	0.17
Gray wooded	–	–	–	2	4.15	0.05	–	–	–	1	3.9	–
All soil zones	11	4.99	0.42	57	4.33	0.34	5	4.14	0.10	32	3.97	0.26
Riboflavin												
Rendzina	–	–	–	1	1.0	–	–	–	–	4	1.08	0.08
Degraded rendzina	–	–	–	1	1.4	–	1	1.2	–	5	1.18	0.04
Black earth	10	1.05	0.17	30	1.12	0.14	4	1.05	0.15	7	1.11	0.16
Black earth–rendzina	–	–	–	1	1.1	–	–	–	–	–	–	–
Dark brown steppe–black earth transition	1	1.2	–	3	1.10	0.10	–	–	–	2	1.15	0.15
Northern black	–	–	–	13	1.18	0.09	–	–	–	6	1.15	0.11
Northern black–gray black	–	–	–	1	1.3	–	–	–	–	–	–	–
Gray black	–	–	–	5	1.18	0.16	–	–	–	7	1.04	0.12
Gray wooded	–	–	–	2	1.10	0.10	–	–	–	1	1.0	–
All soil zones	11	1.06	0.17	57	1.14	0.14	5	1.08	0.15	32	1.11	0.12

variance for these two varieties for rendzina, black earth, and northern black soil zones showed no significant difference of thiamine content between varieties or soil zones.

The content of riboflavin in oats is more uniform than in barley. The averages for varieties differ by only 0.06 μgm. per gm., which is much less than the standard deviation for any one variety. Analysis of variance indicated that differences between varieties, as well as between soil zones, were not significant.

Wheat

Four wheat varieties were assayed for thiamine, as is indicated by the data in the upper half of Table IV. Decreasing amounts of this vitamin as shown by variety averages occur in Carlton, Regent, Renown, and Thatcher. The first of these was grown on only two soil zones, but its value for each of these was higher than for any of the other three varieties grown in the same zone. Since its over-all average is 0.66 μgm. per gm. higher than for the second variety and its standard deviation is 0.12 it would seem to be easily the best of the four. Only five samples of Renown were collected, and from two soil zones, so little can be concluded about it. That the difference between Regent and Thatcher is significant is shown by an analysis of variance for these two varieties grown in seven soil zones. This difference has already been mentioned by Jackson and Whiteside (7) and Whiteside and Jackson (12). At the same time the analysis of variance did not reveal any significant differences between soil zones.

That the riboflavin contents of these four varieties are much the same is shown by a comparison of the averages reported in the lower half of Table IV. The difference of 0.08 between the lowest and highest riboflavin contents is meaningless. This is not in accord with the findings of Andrews *et al.* (3), who reported Thatcher wheat to contain more riboflavin than Renown. An examination of soil zone averages reveals no marked differences for the various zones. The lowest average for a group containing at least two samples is 1.05 μgm. per gm., the highest 1.18. Most standard deviations approach or exceed the difference between these two. Again there is no uniformity in order of riboflavin content by soil zone for the different varieties. These general conclusions were verified by an analysis of variance for riboflavin content of Regent and Thatcher wheats grown on seven soil zones.

Correlation coefficients for thiamine with riboflavin and for each of the vitamins with protein and ash were calculated for each of the three cereals. These values are reported in Table V. There are significant positive correlations between protein and thiamine in oats and barley and between protein and riboflavin in wheat. There is no correlation between protein and thiamine in wheat or between protein and riboflavin in oats and barley. A significant positive correlation is found between ash and riboflavin in barley and a significant negative one between ash and thiamine in oats.

TABLE V

CORRELATION COEFFICIENTS FOR THIAMINE AND RIBOFLAVIN WITH PROTEIN AND ASH

Cereal	Barley	Oats	Wheat
Number of samples	48	54	102
Protein–thiamine	.5042**	.7432**	.0331
Protein–riboflavin	.0949	.1393	.2514**
Ash–thiamine	—.0993	.3016*	—.0038
Ash–riboflavin	.3641*	.0886	.1572
Thiamine–riboflavin	.0718	.1580	.0663

**Within 5% level of significance.*
***Within 1% level of significance.*

The lack of a significant correlation between thiamine and either protein or ash in wheat is in harmony with the findings of Johannson and Rich (8), though contrary to those of McElroy *et al.* (9), who found one for protein and thiamine. These authors report one for protein and thiamine in oats, which is confirmed by our results. Their results did not show one for protein and thiamine in barley, whereas the one obtained in this investigation is within the 1% level of significance. The lack of a significant correlation for ash and thiamine in wheat confirms the earlier report of Nordgren and Andrews (10) who found none for winter wheats or Western Canadian spring wheats, though they did for American-grown spring wheats. Our not obtaining a correlation between riboflavin and protein in barley and oats confirms the results of McElroy and his coworkers, but the one between riboflavin and protein in wheat does not.

The significant correlations are of interest and may indicate a causal relation. The values are too small to permit the prediction of vitamin contents from ash or protein ones.

Acknowledgments

Grateful acknowledgment is made to Mr. Whiteman and the District Representatives of the Extension Service of the Manitoba Department of Agriculture, and to Mr. D. A. Brown of the Brandon Experimental Farm for the collection of samples; and to Prof. J. H. Ellis of the Department of Soils, University of Manitoba, who identified the soil zones where the samples were grown.

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A SIMPLE ELECTRICAL METER FOR ESTIMATING THE MOISTURE CONTENT OF GRAIN[1]

H. E. RASMUSSEN[2] AND J. A. ANDERSON[3]

Abstract

A simple electrical meter has been devised for estimating the moisture content of grain. It accommodates a 190 gm. sample which forms the dielectric of a condenser in the plate tuning circuit of a triode crystal oscillator. An increase in the dielectric constant due to moisture in the sample is compensated for by removing capacity from a variable condenser attached to the dial of the instrument. A piezoelectric plate determines the frequency at which the triode section of the tube will oscillate, and this state is indicated by a change in the shadow angle of the indicator section of the same tube. The meter has been calibrated with 159 samples of Canadian hard red spring wheat; the standard error of estimate was found to be 0.36 over the range from 10 to 17% moisture.

A number of electrical meters for estimating the moisture content of grain by measuring electrical properties are now commercially available. In most of these, the dielectric constant of the grain is determined by frequency deviation or phase shift methods which involve relatively complex circuits and the use of accurate indicating instruments. The meters are therefore expensive. A meter with a simpler electrical circuit, which it should be possible to manufacture and market more cheaply, was devised by one of us (H.E.R.) in 1945. A similar circuit has since been described by Fischer (1). The G.R.L. meter (christened with the initials of this Laboratory) is described in the following three sections dealing with design, circuit, and operation.

General Design

A photograph of the instrument is shown in Fig. 1. All components are attached to an etched metal panel supported on an oak case which houses the measuring circuit and power supply. The rectangular tube at the back of the photograph (inside dimensions, 10 by 5.5 by 0.75 in.) extends about equally above and below the panel. It has spring-loaded horizontal gates in the center and at the bottom, and thus provides a loading hopper and a measuring cell. A white push knob for opening the gate that dumps grain into the cell is shown at the left of the hopper; a corresponding knob on the right controls the gate that empties the grain from the cell into the drawer in the end of the oak case. Small black knobs at front and back are the power switch and fuse mount. The main dial of the instrument is shown at the front. Between this and the hopper there is a shield which protects the top of an electronic tube that indicates, by a change in the shadow angle,

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Paper No. 97 of the Grain Research Laboratory, Board of Grain Commissioners for Canada, Winnipeg, Manitoba, and No. 269 of the Associate Committee on Grain Research.
[2] *Senior Technician.*
[3] *Chief Chemist.*

when the dial has been correctly adjusted in making a reading. Other mechanical details are not described because they are relatively unimportant and will doubtless be changed if the meter is redesigned for factory production.

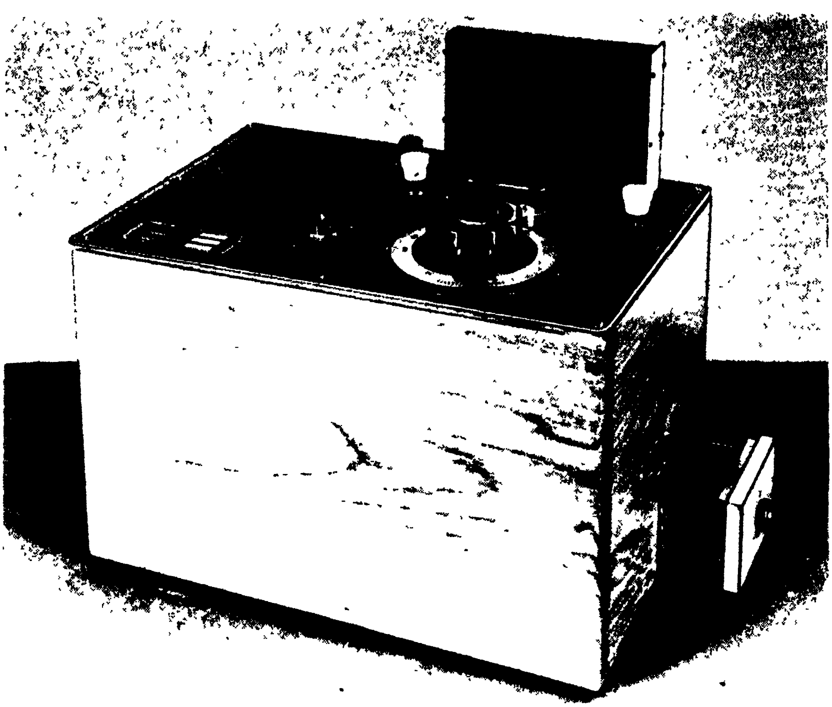

FIG. 1. *Photograph of G.R.L. moisture meter.*

Electrical Circuit

The circuit is shown in Fig. 2. A 6E5 electron ray indicator and triode tube T has the plate circuit tuned to the frequency (7.3 Mc.) of a piezoelectric plate by a resonant circuit consisting of an inductance L and three condensers, C_1, C_2, and C_3, in parallel.

Variable condenser C_1 (30 $\mu\mu$f.) can be set with a screwdriver and is used merely to compensate for unpredictable interelectrode and distributed capacitances of the circuit components. Variable condenser C_2 (15 $\mu\mu$f.) has attached to it the dial of the instrument, and its capacitance can thus be varied to tune the plate circuit. Each dial division represents 0.144 $\mu\mu$f. capacitance. The condenser C_3 is a dielectric cell in which the grain is placed. It consists of two aluminum plates, 8.9 cm. by 12.0 cm., spaced 1.9 cm. apart, attached to the insides of the bakelite walls of the rectangular tube previously described. Capacitance at the terminals of the cell, when empty, is 17.0 $\mu\mu$f.

When grain is placed in the cell, the capacitance is increased by an amount which is a function of the moisture content of the grain. The dial is then turned to remove capacitance from C_2 until the product L $(C_1 + C_2 + C_3)$ attains the value at which oscillation begins. The decrease in plate current through the resistor R (100,000 ohm) then causes an abrupt increase in the shadow angle of the indicator section of tube T. When this change is observed, the position of the dial is read on an arbitrary scale.

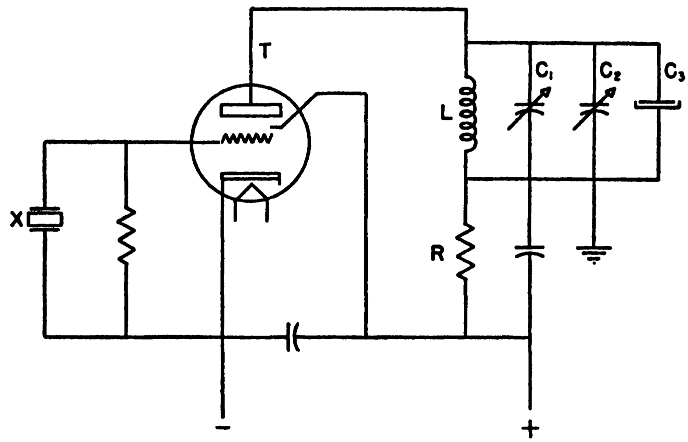

FIG. 2. *Circuit for G.R.L. moisture meter.*

Owing to the very high Q of the oscillator grid circuit, the value of plate tuning capacitance at which the crystal begins to oscillate is critical, especially when approached from the capacitive side. Once oscillations have started, a larger change in plate tuning capacity is necessary before the circuit drops out of oscillation. Accordingly, the point of balance must be approached slowly, so that the meter reading will represent the beginning of oscillations.

Power is obtained from a full wave rectifier, a resistance capacity filter, and a pair of voltage regulating tubes. The instrument is designed for 115 v. a-c., but variations of $\pm$ 10 v. do not affect its operation. Alternatively, power could be readily supplied by batteries or Vibropack.

Operation

Before making a reading, the power must be turned on and the instrument allowed to warm up for five minutes. The dial is then turned anticlockwise against a mechanical stop. A 190 gm. sample of wheat, the temperature of which must be known, is poured into the hopper and roughly leveled. Sharp depression of the loading knob dumps this grain into the cell under conditions that ensure uniform packing. The dial is then turned clockwise until the shadow angle of the indicator tube opens. For the most accurate reading, the dial should then be turned back so that the estimated equilibrium point

can be approached more slowly. Dial readings are converted to percentage moisture by referring to a chart, and the converted reading is subsequently corrected for temperature.

The meter has been calibrated with 159 samples of hard red spring wheat taken from carlot shipments made during the 1947-48 crop year. Moisture determinations were made on duplicate subsamples by preliminary drying at room temperature, grinding, and drying overnight in a vacuum oven at

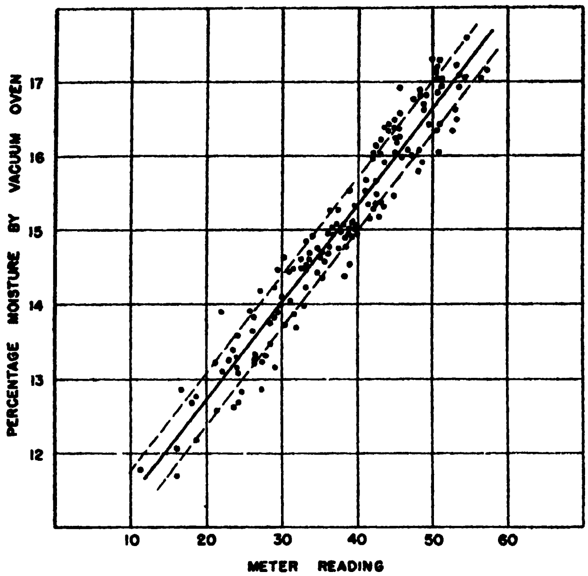

FIG. 3. *Scatter diagram showing relation between moisture contents of wheat determined by the vacuum oven method and by the G.R.L. moisture meter.*

100° C. Meter readings were made on duplicate subsamples in a room maintained at 72° ± 0.5° F. in which both meter and samples had been held for at least two days. Fig. 3 shows the resulting scatter diagram for the plot of vacuum oven moistures against meter readings. The regression equation is: vacuum oven moisture = 0.132 × meter reading + 10.06; the standard error of estimate is 0.36% moisture. A preliminary study of the effect of temperature indicates that the correction is 0.06% per 1° F.; this is added for temperatures above and subtracted for temperatures below 72° F.

This study comprised part of a larger investigation in which nine meters were compared; a paper on this work is in preparation for early publication. The G.R.L. meter ranked fourth in accuracy. Errors of estimates for the remaining eight meters were 0.23, 0.28, 0.35, 0.41, 0.45, 0.48, 0.49, and 0.58. The two most accurate instruments measure resistance; so that the G.R.L. meter, in spite of its simplicity, is essentially equal in performance to the best dielectric moisture meters tested in this laboratory.

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FROZEN STORAGE OF POULTRY

V. EFFECTS OF SOME PROCESSING FACTORS ON QUALITY[1]

BY JESSE A. PEARCE[2] AND C. G. LAVERS[3]

Abstract

Examination of a number of phases of poultry processing showed that birds of optimum quality were obtained by: using a 90 sec. bleeding time; dipping in a semi-scald tank for 40 sec. at 128° F., operating both shafts of the rough-plucker at the same speeds, operating the rough-plucker at conditions such that the rubber fingers did not exert a force greater than 11 lb. on the carcass, and carefully training operators of hand-roughers. Splitting the carcasses up the back, eviscerating, and packing flat reduced the space required for packing to less than 50% of that required by present methods, and still permitted reassembly of the bird into a presentable form for roasting. An impact dynamometer was useful in detecting unfrozen spots in the birds. Injecting various solutions into the carcass before freezing, and measuring the drip from the defrosted muscle, showed that maintaining the proper ratio of salts and water in the muscle reduced drip. Bleeding time had no effect on development of off-odors in stored poultry but evisceration before storage markedly reduced development of off-odor on the eviscerated surface and in the thigh meat. Coating eviscerated birds before freezing with carrageenin gel containing 6% sodium chloride delayed development of off-odor on eviscerated surfaces of defrosted carcasses.

Introduction

Earlier papers in this series described the effects of precooling, rates of freezing, and frozen storage on the quality of poultry. However, little published information is available with respect to effects of killing and plucking procedures on quality of frozen poultry. The present paper describes studies on effects of different intervals between killing and entry into the semi-scald tank on dressing out and keeping qualities; detection of unfrozen cores in carcasses; methods that reduce the space required for packing and storage; and preservation of the eviscerated surface after defrosting.

Methods

Many of the appraisals were subjective, and, since they dealt with factors affecting the grading, were made by inspectors of the Dominion Department of Agriculture according to Canadian regulations (2). Other subjective appraisals were made by taste panels recruited from the staff of the National Research Laboratories.

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[2] *Biochemist, Food Investigations.*

[3] *Formerly Chemical Engineer, Food Investigations. Present address: Research Department, Maple Leaf Milling Co., Toronto, Ont.*

The various quantitative methods are described in those sections in which they were used.

The procedure used in dressing poultry in many Canadian processing plants and used in this study is briefly as follows. The birds are killed, allowed to bleed for a short period (bleeding time) passed through a tank of violently agitated warm water (semi-scald tank), and then between the rotating shafts of an automatic rough-plucker where hollow rubber fingers beat off most of the feathers. The fingers, about $8\frac{1}{2}$ in. long and 5/8 in. in diameter, are placed in rows on the shafts, which are about $5\frac{1}{2}$ in. in diameter. The feathers remaining after rough-plucking are removed by a hand-rougher or by hand. The hand-rougher usually consists of a revolving drum, about 22 in. in diameter, with rubber fingers about 4 in. long on its surface. The shape of these fingers varies—some are circular and hollow, others are square and solid. The birds are held against these fingers by hand and the remainder of the coarse feathers are removed. After the birds leave the hand-rougher, pin-feathers are removed by hand.

Some plants have additional equipment for eviscerating birds, but in these studies, evisceration was done in the laboratory by hand.

Prefreezing Processing

Effect of Bleeding Time on Quality

In this phase of the study, the intervals allowed between killing and entry of the carcass into the semi-scald tank were 30 and 90 sec., since the use of longer or shorter times or of more than two time intervals caused too much

TABLE I

EFFECT OF 30-SEC. AND 90-SEC. INTERVALS BETWEEN STICKING AND SEMI-SCALDING ON PROCESSING DEFECTS IN POULTRY

Defect	Defective birds, %	
	30-sec.	90-sec.
Chicken		
Poor feather removal	12.8	1.5
Scalding	55.5*	45.0*
Rubbing	52.0	39.7
Skin bleeding	43.3	15.2
Fowl		
Poor feather removal	9.2*	8.2*
Scalding	31.7*	29.4*
Rubbing	33.6	18.2
Skin bleeding	7.3	1.2

**No significant difference between the values for the 30-sec. and 90-sec. intervals.*

inconvenience in the commercial plant. Unfortunately, the automatic control on the semi-scald tank was not operating on the day of this trial, and the temperature in the tank had to be controlled by hand. This resulted in temperature variation in the water from 128° to 132° F. The birds remained in the tank for 45 sec. One shaft of the rough-plucker was turning at 330 r.p.m. and the other at 290 r.p.m. The hand-rougher was operated at 360 r.p.m.

In all, about 800 birds were processed, about 400 at each bleeding time. The results (Table I) showed that birds classed as chicken suffered more defects than birds classed as fowl. For chicken, the short bleeding time reduced the efficacy of feather removal by the rough-plucker. On the other hand, feather removal was impossible if bleeding time was prolonged for five minutes. Rubbing, i.e., abrasion of the skin by the rubber fingers, was greater in birds bled for 30 sec. and is believed to be a direct reflection of the increased handling required to remove feathers on the hand-rougher. A 90 sec. bleeding time effectively reduced the incidence of skin bleeding. In general, these results show that a 90 sec. bleeding time is more desirable than a 30 sec. bleeding time, and for chicken in particular, a 90 sec bleeding time effected a marked reduction in the number of feathers that must be removed by the hand-rougher.

TABLE II

EFFECT OF TEMPERATURE AND TIME IN SEMI-SCALD TANK ON FORCE REQUIRED TO REMOVE FEATHERS FROM POULTRY

(10 to 40 birds processed at each condition)

Temp., °F	Time, sec	Force, oz		
		Plant A	Plant B	
		Chicken	Fowl	Chicken
125	30	15	22	24
	40	13		15
	50			15
128	20	12		
	30	14	20	23
	40	15		11
130	20			9
	30			11
132	15	13		10
	20	16		
	30	8		
	40	7		
134	15	15		
	20	8		
136	15	5		

Effect of Time and Temperature in the Semi-scald Tank

The time that birds are in the semi-scald tank and the temperature of the water affects not only the quality of the dressed birds but also the effectiveness of the plucking operations.

Table II shows the effect of conditions in the semi-scald tank on the average force required to remove small feathers from the wings and tail (feathers clamped to spring scale). Work was done at Plant A early in September, when birds were still moulting. Relatively little force was required to remove the feathers, and excessive times and temperatures were necessary to effect any reduction in force required. Work was done in Plant B in late November, and, at the lower temperatures and shorter dipping times, the force required to remove the feathers was generally much higher than for September birds. The effect of time of year on the ease of feather removal requires more study. However, for the two periods studied here, approximately uniform resistance might be obtained by the use of appropriate dipping times and temperatures. In general, these results show that the force required to remove feathers from the birds is reduced by increasing the water temperature in the semi-scald tank and by increasing the time of dipping.

Table III shows that the effect of semi-scald tank operation on damage (combined scalding and rubbing) to the carcass is complicated by plucking operations. In Plant A, the birds were examined after passage through a rough-plucker with shafts rotating at 380 r.p.m. and a hand-rougher operating at 130 r.p.m. In Plant B, the birds were examined after passage through a rough-plucker only, with shafts turning at 360 r.p.m. Birds processed in Plant A at the intermediate temperatures showed least damage at the longest dipping times, while birds processed in Plant B showed greatest damage at the longest dipping times. This discrepancy was apparently due to the use of the hand-rougher in Plant A. At the longer dipping times, feathers were more easily removed by the hand-rougher, which reduced the damage from rubbing. From these results and the results in Table II, dipping for 40 sec. in a tank containing water at 128° F. seemed most desirable, if the operation of the two types of pluckers was satisfactory.

Effect of Plucker Operation on Quality

This study was made in only one plant. To eliminate damage from scalding, the water in the semi-scald tank was at 125° F. and the dipping time 30 sec. This temperature and time combination is lower than that recommended in the previous section and feather removal in the rough-plucker was less complete.

Table IV shows that the amount by which the rubber fingers overlap, from a gap of $2\frac{1}{2}$ in. to an overlap of $3\frac{1}{2}$ in., had little effect on rough-plucker operation but that the two shafts had to be operated at the same speed if excessive rubbing was to be avoided. If the shafts were operating at the same speed, the least rubbing damage occurred when the rubber fingers did

TABLE III

EFFECT OF TEMPERATURE AND TIME IN SEMI-SCALD TANK ON FEATHER REMOVAL AND DAMAGE

(10 to 40 birds examined at each condition)

Temp., °F	Time, sec.	Plant A	Plant B	
		Birds damaged, %	Feather removal	Birds damaged, %
125	30	10	Fair	10
	40	50	Good	58
128	20			
	30	60	Good	50
	40	25	Good	80
130	20		Good	66
	30		Good	90
132	15	100	Fair to Good	81
	20	80		
	30	85		
	40	66		
134	15	55		
	20	90		
136	15	100		

TABLE IV

FACTORS IN ROUGH PLUCKER OPERATION AFFECTING FORCE ON THE BIRD, FEATHER REMOVAL AND DAMAGE

(10 to 40 birds examined at each operating condition)

Rough plucker			Maximum downward force on birds, lb.	Feather removal	Damaged birds, %
Speed, r.p.m.	Overlap of fingers, in.				
	Entrance	Exit			
Shafts at same speed					
270	2½	0	7.0	Poor	0
	3½	1½	8.0	Poor	0
360	0	0	8.8	Fair	20
	1	1	10.6	Fair	10
440	2½	0	13.6	Good	85
Shafts at different speeds					
330, 340	1	0	9.8	Fair	80
	3½	1½	7.4	Fair	77
380, 410	0	−2½	11.2	Good	75
	2½	0	13.3	Good	77

not exert a maximum force (measured by a spring scale) of more than about 11 lb. on the bird's carcass.

Table V shows that use of the hand-rougher (335 r.p.m.) under semi-scalding conditions approximating those described above doubled the damage to both chicken and fowl. Since little mechanical change can be made in this hand-rougher, the operators must be given special training in its use to avoid excessive damage at this stage of the operation.

TABLE V

EFFECT OF HAND PLUCKER ON DAMAGE TO BIRDS
(30 birds of each type examined at each operating condition)

Equipment used	Birds damaged, %	
	Chicken	Fowl
Rough plucker only	36	42
Rough and hand plucker	62	83

Packing Poultry for Freezing

Current methods of packing poultry waste space, so it was of interest to examine other methods. For this purpose, New York dressed birds weighing 60 lb. per doz. were used, which, by current packing methods, require a box with inside dimensions of 24 by $14\frac{1}{2}$ by $7\frac{1}{2}$ in., i.e., approximately 2600 cu. in. (Fig. 1). Eviscerating the birds and removing the heads and feet reduced the size of the box required to 24 by $14\frac{1}{2}$ by $5\frac{1}{2}$ in., i.e., to approximately 1900 cu. in.

Further comparisons were made using eviscerated birds. Various methods, based on cutting the bird through the center of the ventral cavity or on cutting the bird completely in half, were tried and discarded, since the bird could not be reassembled to make presentable roast chicken and since the breast muscles were exposed with the added danger of spoilage in the most meaty portion of the bird. Splitting birds up the back reduced the time required for evisceration and permitted easy reassembly for roasting, but packing with the back halves of two birds in the body cavity of the third saved little space.

Cutting the birds up the back and flattening by cracking the ribs provided packing in a minimum of space and still permitted reassembly into a presentable form for roasting. Two methods of packing were selected from the large number possible. In the first, the flattened birds were packed on edge with the neck or thighs alternately toward the bottom of the box. This pack required a box with internal dimensions of 21 by 8 by $9\frac{1}{2}$ in., i.e., approximately 1600 cu. in. In the second (Fig. 2), the birds were packed in three columns with the breast surface of one bird in the eviscerated cavity

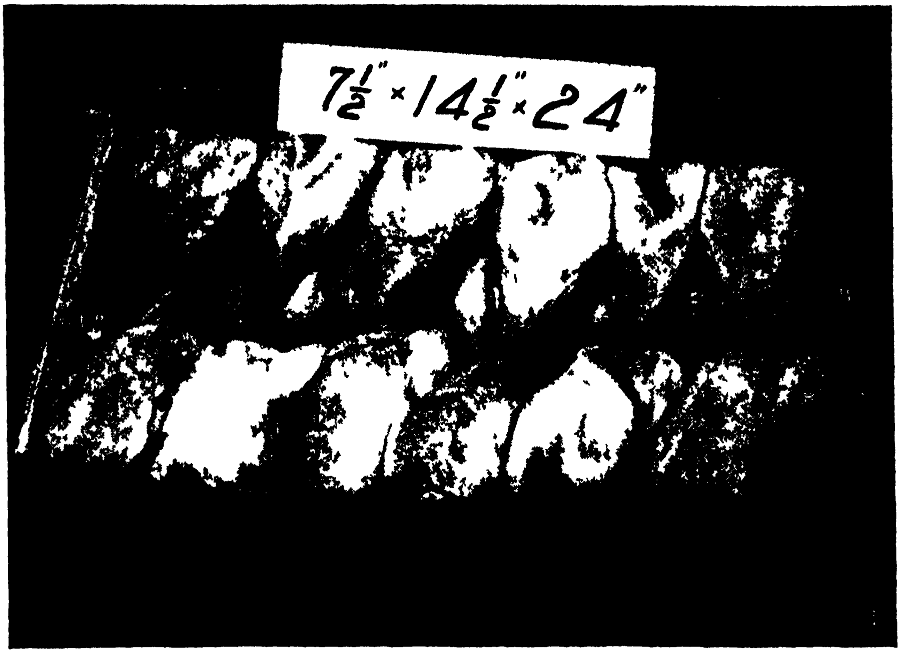

FIG. 1. *Current method of packing poultry; weight of birds, 60 lb. per doz.*
FIG. 2. *A suggested method of packing poultry; weight of birds, 60 lb. per doz.*

of another. Necks and legs in each row were alternated to reduce the space required. This pack fitted into a box with internal dimensions of 21 by 8 by 7½ in., i.e., approximately 1250 cu. in.

Both of these methods effect considerable saving in space and in packing material but have some disadvantages. In the common method of packing, the frozen birds can be separated fairly readily for sale, but in both the suggested methods the birds freeze into a solid block and cannot be separated readily unless completely defrosted, or unless two sheets of a light, dry-waxed paper are placed between the birds. The first of the suggested methods presents an unsightly appearance because of the protruding necks and joints; the second suffers from an objection to piling birds on top of each other. Neither method permits easy grading. However, these disadvantages are offset by the advantages; ease of evisceration, saving in packing material, and saving in space. In addition, the reduction of exposed surface should help reduce the freezer-burn that occurs during extended storage periods.

Freezing Poultry

Measuring Freezing

Several studies of factors affecting freezing rates in poultry have been made (5; 6; 7; 9, p. 438) and, in these, freezing time was defined as the time required for the temperature to be reduced by a definite amount. Development of a dynamometer for testing hardness and depth of freezing in frozen foods (8) permitted a comparison between these factors and freezing time as assessed by conventional temperature measurements.

In this phase of the study, three- and five-pound birds at about 31° F. were hung at intervals of 1 ft. in rooms operating at − 28°, −10°, 0°, and 20° F., with gentle air motion. Thermocouples were placed in the centers of the birds and the freezing time was that required to attain a temperature of 20° F. in the center of the bird. If poultry flesh is similar to the flesh of other animal products (6) about 10% of the water would still be unfrozen at this temperature. Freezing times by this method were determined with a standard deviation of ± 0.6 hr. and were, therefore, considered satisfactorily reproducible.

Dynamometer measurements were made at each sampling time in three parts of the birds' carcass: in the breast area, between the lower ribs, and in the abdomen. There was little difficulty in allowing for passage of the dynamometer through the bones; but air cavities in the viscera were a problem, since they offered no resistance to the dynamometer. The best point for measurement appeared to be between the lower ribs, but the results presented here are the average for all three sets of readings.

The temperature measurements (Fig. 3) showed that increasing the temperature of the freezing chamber from − 28° to 0° F. increased the freezing time from 5 to 12 hr; at 20° F. the freezing time was about 48 hours.

The times in which the birds were frozen to any fixed depth (assessed by the dynamometer) paralleled the freezing time; and the hardness of the frozen portion, as measured by resistance to dynamometer penetration, increased uniformly as freezing progressed at any given temperature. The marked variation in hardness of birds frozen at different temperatures had no effect

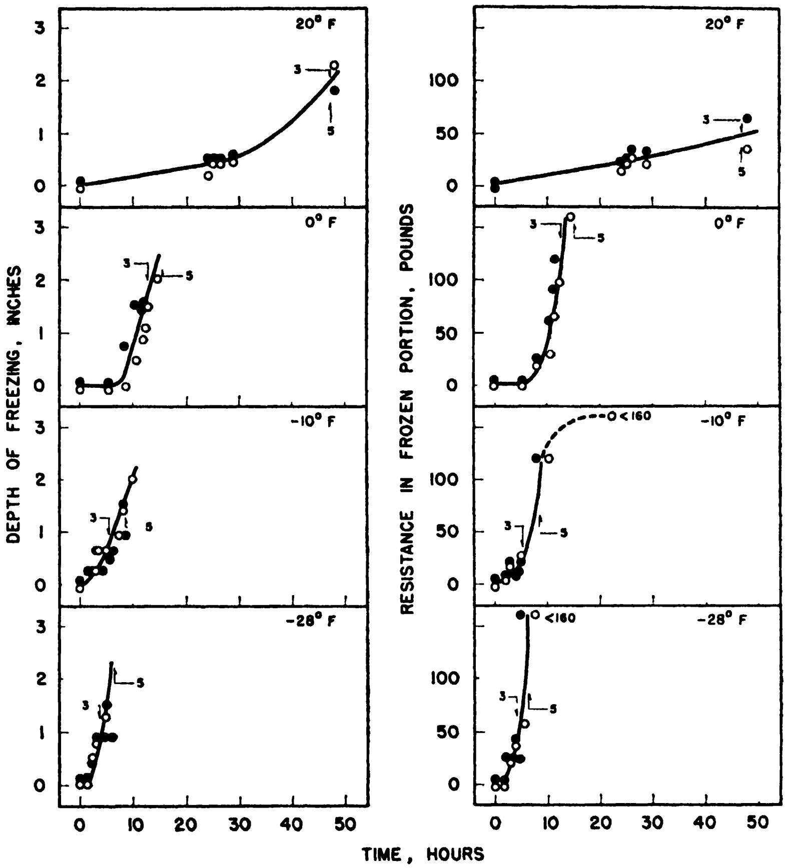

FIG. 3 *The freezing of 3-(o) and 5-(•) lb chicken carcasses, as assessed by an impact dynamometer, and as related to the time for the center of the carcass to reach 20° F determined with thermocouples arrow marked 3, point at which 3-lb birds reached this temperature, arrow marked 5, point at which 5-lb birds reached this temperature*

on the detection of unfrozen portions, which have no resistance to the dynamometer. It was concluded that, for poultry, the usefulness of the dynamometer will probably be confined to the detection of unfrozen spots in the carcasses.

Reducing Drip in Frozen Poultry

Studies elsewhere (7) have shown that open canals or vacuoles may be retained in muscle fibers by fast freezing. This retention of vacuoles was believed to be an indication of intrafibrillar freezing. Vacuoles may be present in the muscle fibers of live or freshly killed birds, although they may

not be detected by present histological techniques. Their presence in the muscles of rapidly frozen birds (7), and the reduced drip in defrosted birds that have been frozen rapidly (5), may be an indication that rapid freezing is necessary to preserve the vacuoles and, thereby, to reduce drip from the muscles after defrosting by retaining the fluid in vacuoles. If this is so, fluid might be retained by other procedures, such as the injection of solutions that would reduce pH changes, or alter the diffusion of ions that normally occurs in dead muscle tissue. This problem was examined by introducing various solutions into the birds' muscles, allowing the birds to stand for about an hour before freezing in about five hours, and by measuring drip after defrosting.

The solutions used were: water, 10^{-4} N ammonium hydroxide, phosphate buffer at pH 7.2 (3, p. 200), and Tyrode's modification of Ringer's solution (1, p. 257). The number of aliquots in any part of a carcass was roughly proportional to the amount of muscle believed to be in that portion of the bird and to a limiting amount of 30 ml. per lb. of muscle; i.e., its moisture content would be increased from approximately 70% to 85%. Each solution was used on groups of four birds; in addition four birds were frozen without injection, and four unfrozen birds were examined.

Drip was measured as the per cent decrease in weight by a technique similar to that described elsewhere (5) except that the right and left chest and thigh muscles were dissected from the frozen bird and drip measured without mincing.

The data were subjected to statistical analysis and the results are given in Table VI. Chest muscles lost a significantly greater quantity of fluid

TABLE VI

EFFECT OF ADDING 30 ML. OF VARIOUS SOLUTIONS PER LB. OF BIRD, BEFORE FREEZING, ON THE AMOUNT OF DRIP IN DEFROSTED POULTRY MUSCLES

(Four birds given each treatment)

Treatment	Amount of drip, %		
	Chest	Thighs	Average
Unfrozen			
None	2.5	1.4	2.0
Frozen			
None	3.4	2.0	2.7
Water	5.4	4.0	4.7
Ammonium hydroxide	5.0	4.6	4.8
Phosphate buffer	4.6	4.2	4.4
Tyrode's solution	4.1	3.6	3.8
Necessary difference, 5% level			0.8
Average	4.2	3.3	

than thigh muscles, but, although frozen untreated muscle exuded more fluid than unfrozen muscle, the difference was not statistically significant. The injection of water into muscle caused a marked increase in drip, but a large portion of the added water was retained by the muscle. The use of Tyrode's solution gave a product with significantly less drip than that containing added water, indicating that retaining the proper ratio of salts and water in muscle may help to retain its structure during freezing. Evidence of vacuoles was found in frozen sections of only the muscles injected with Tyrode's solution.

Retaining Quality After Freezing

Frozen Storage

Poultry in chill or frozen storage develops an undesirable odor in the flesh of the thigh. It has often been suggested by processors and others that this odor was attributable to the short interval that elaspes between killing the bird and introducing it into the semi-scald tank. It was believed that the bird entered the water with its heart still beating, that the dirty semi-scald water containing bacteria was pumped through the veins and arteries, and that, during storage, bacteria retained in the thigh caused the off-odor On the other hand, the possibility exists that off-odors come from the viscera, as only a thin membrane separates the viscera from the meat in the thigh.

To examine this question, Grade A fowl processed in an earlier phase of this study were stored at 0° and 30° F. and examined at the intervals shown in Fig. 4. Forty birds had been subjected to the 30-sec. bleeding time and 40 birds to the 90-sec. bleeding time. Each group of birds was divided into four lots: two lots from each group were eviscerated; one lot of eviscerated and one lot of noneviscerated birds from each group was stored at each temperature. At each sampling time random pairs of birds were drawn from each lot and group, and the bacterial count in the thigh muscles was determined. All the birds were submitted to a taste panel of 24 persons who smelled the eviscerated surface and the thigh meat and scored it according to a scale from 0, no off-odor, to 5, gross off-odor.

The viable bacterial count varied from 10^2 to 10^3 per gm. of thigh meat and did not change during storage at either temperature.

The taste panel data were subjected to statistical analysis and the significant results are given in Fig. 4. They showed that bleeding time had no effect on the development of off-odor either on the eviscerated surface or in the thigh meat, but that off-odors increased rapidly in the viscera and were transmitted to the thigh meat. Therefore, eviscerating seems to be a desirable step in processing frozen poultry.

Storing Defrosted Birds

The eviscerated surface of poultry is usually believed to deteriorate rapidly unless the carcass is frozen, and this deterioration is reputed to be more rapid in defrosted birds than in birds that have never been frozen. Therefore,

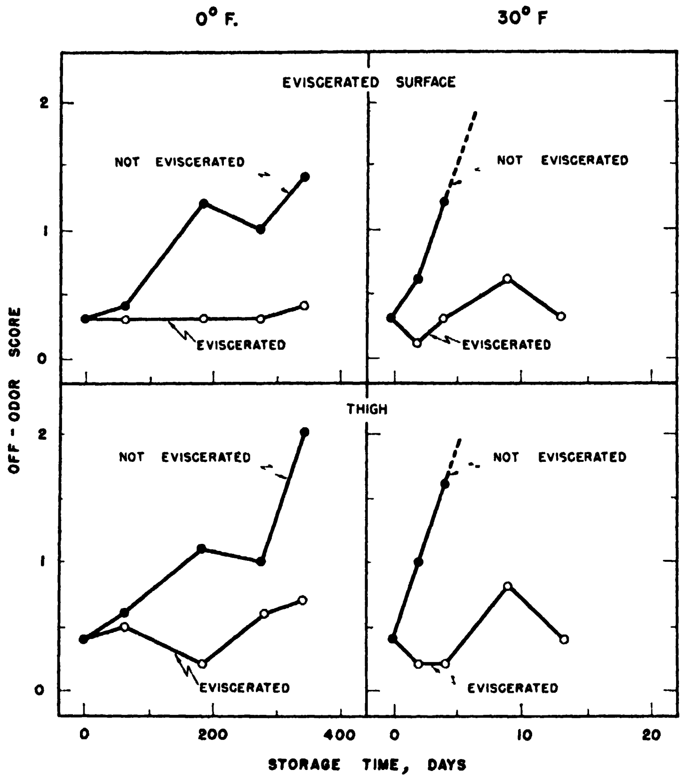

FIG. 1. *Change in off-odor on the eviscerated surface and in the thigh of eviscerated and non-eviscerated fowl stored at 0° and 30° F.*

it was of interest to determine the storage life of defrosted birds held at temperatures of 40°, 60°, and 80° F. and to examine possible methods of extending storage life at these temperatures.

For this study, birds weighing 60 lb. per dozen were eviscerated and treated before freezing as shown in Table VII. Wrapping was done by heat-sealing

TABLE VII

STORAGE LIFE, HR., OF DEFROSTED EVISCERATED POULTRY TREATED IN VARIOUS WAYS AND HELD AT DIFFERENT TEMPERATURES

Treatment	Temperatures, °F.		
	40	60	80
None	120	31	12
Partial cook	120	16	8
"Cellophane" wrap	48	25	12
Sodium benzoate dust	120	31	12
Butyl ester of *p*-hydroxybenzoic acid dust	120	31	12
Calcium proprionate dust	120	48	34
Carrageenin gel coat	168		
Carrageenin gel coat (4% sodium chloride)	168	72	
Carrageenin gel coat (6% sodium chloride)	192	83	32

the birds in 450 M.S.Y.T. "Cellophane". Carrageenin gel, an extract of Irish moss seaweed, was applied by dipping the birds into solutions, at 212° F., consisting of 4% of a 4 to 1 mixture of carrageenin and potassium chloride (4) to which 0, 4, and 6% of sodium chloride was added. The eviscerated birds were partially cooked by placing them in a chamber which was brought to 212° F. in 15 min. and held at that temperature for 30 min. The dry chemicals were dusted on the eviscerated surface only. Off-odors on the eviscerated surface were scored on a scale from 0 (good) to 4 (very badly off) and a score of 2 was considered the limit at which the birds would be suitable for table use. The numbers of viable bacteria on the eviscerated surface were determined at intervals, but the counts were too irregular to be of value.

Table VII shows the time in hours required for the birds to reach an off-odor score of two. Unwrapped, untreated birds kept for 120, 31, and 12 hr. at 40°, 60°, and 80° F. respectively. Wrapping in Cellophane or partial cooking caused more rapid deterioration than holding untreated birds in the open. Dusting with dry chemicals had no effect. Coating the birds with carrageenin gel containing 6% sodium chloride approximately doubled the storage life. The gel is easily removed, and in this study, as in another study of the use of salt for preserving quality in unfrozen birds (10), the salt did not affect the palatability of the flesh.

Acknowledgments

The authors wish to express their thanks to the many persons who assisted with various phases of this study, and special thanks to Mr. E. D. Bonnyman and his inspectors in the Special Products Board of Marketing Service, Department of Agriculture (Canada). The managers and staffs of the Ottawa and Smith Falls, Ontario, plants of Canada Packer's Limited, and the manager and staff of Le Co-operative des Produits Avicoles at Marieville, Que., also gave full co-operation throughout the work.

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A SEMIQUANTITATIVE METHOD FOR THE DETECTION OF ACETIC ANHYDRIDE IN ACETIC ACID[1]

By G. Benson[2] and R. M. Kitchen[3]

Abstract

When acetic acid is handled in aluminum it is important for reasons of corrosion resistance that the acid be not completely anhydrous, a condition that results if traces of acetic anhydride are present. A quick colorimetric test depending on the reaction between acetic anhydride with aniline has been developed by which it is possible to detect 0.05% acetic anhydride in acetic acid.

In the manufacture, shipment, and use of glacial acetic acid considerable use is made of aluminum vessels and pipe lines, the corrosion resistance of which is very good when, as is normal, the acetic acid contains traces of water. In perfectly anhydrous acetic acid, however, the rate of corrosion is quite rapid (5, 6) and care must be taken in industrial practice to ensure that anhydrous acetic acid does not come into prolonged contact with aluminum. The only circumstances under which anhydrous conditions are likely to be produced and maintained is by the addition of acetic anhydride to acetic acid. The rate of corrosion of aluminum by acetic anhydride is greater than that by glacial acid (*c.* 99.7% acid) but is much smaller than the rate by anhydrous acid. From the corrosion standpoint therefore, it is the presence of small amounts of acetic anhydride in acetic acid that is particularly undesirable.

The curve shows the rate of corrosion of aluminum in the boiling liquid plotted against acidity expressed as acetic acid, 100% acetic anhydride being therefore represented by 117.6% acidity.

These results were obtained by boiling weighed samples of sheet aluminum totally immersed in mixtures of the acid with anhydride or with water in a flask fitted with a reflux condenser attached to a drying tube, and reweighing after intervals varying from one to several days. The approximately 100% acid was obtained by adding 1% acetic anhydride to 99.9% acid and in this solution the metal sample completely disintegrated in a few days.

Acetic acid is usually estimated by freezing point or by direct titration. The former will, of course, not distinguish between water and acetic anhydride as an impurity. Titration will permit of this distinction but very careful analytical technique is required, since the titration figure obtained in the presence of 0.1% acetic anhydride will differ from that for 0% anhydride by less than 0.02%.

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[2] *Director of Plant Research.*
[3] *Assistant Works Chemist.*

Acetic anhydride may be determined by direct titration or by the difference between total acidity and acidity after reaction with aniline. The second method also requires many precautions and has been found to be quite inadequate for the rapid estimation under plant conditions of small percentages of acetic anhydride.

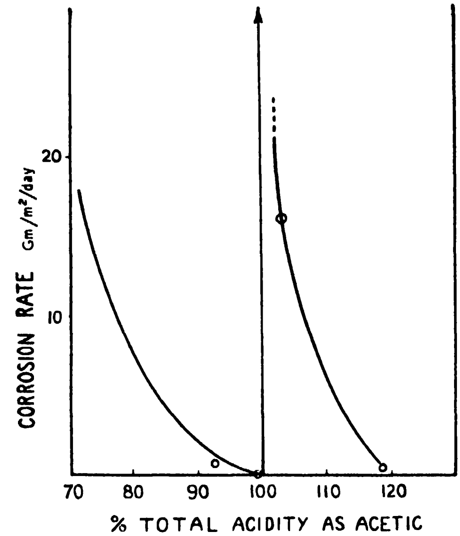

FIG. 1 *The corrosion of aluminum by acetic acid—water and acetic acid—acetic anhydride*

For the measurement of low concentrations of acetic anhydride methods have been described in the literature involving reaction with dichloraniline followed by extraction with chloroform (3), or by determination of excess dichloraniline with bromide-bromate solution (2). Both are accurate but take longer than is desirable. A colorimetric test depending on the Liebermann-Burchard reaction for cholesterol (1) is not sufficiently sensitive

Strength of acid, %	Corrosion rate, gm /m ²/day
50	50
64	12 3
92	0 8
99 7	0 03
100	287
103 5	16 5
116 5	1 5
118	0 7

The following method, depending on the reaction of acetic anhydride with aniline followed by a colorimetric test for free aniline by its reaction with furfural (4), was developed. In the hands of relatively unskilled analysts it will detect 0.5% acetic anhydride in acetic acid and with practice the limit

of detection can be reduced to one-tenth this amount. The color reaction of aniline with furfural was found to be more sensitive in this application than other more common tests.

Experimental

Two reagent solutions are required, one of 5% aniline in pyridine, and one of 1% redistilled furfuraldehyde in acetic acid.

If less than 0.5% anhydride is present in the acid, 1 ml. of the aniline solution is mixed with a 10 ml. sample and allowed to stand one minute. Then 1 ml. of the furfural solution is added. If no anhydride or less than 0.5%, is present in the acid a cherry-red color develops. If 0.5% or more of anhydride is present, a faint straw color will develop.

A test may be made for as little as 0.05% anhydride by using only 0.1 ml. of the aniline solution for a 10 ml. sample. In this case, of course, the color developed by a negative sample is much less intense.

The acetic anhydride in a sample may be estimated to within ±0.05% by using sufficient aniline to develop a color and choosing the best match to this color with the color from a series of standards, which should be freshly prepared, containing 0.0, 0.1, 0.2%, etc. anhydride.

However, we have generally found it sufficient to use the test as a limit gauge at a selected anhydride concentration such as 0.2%, using such quantities of aniline that no color will be developed if the anhydride be above this limit.

The following substances have been found not to interfere with the test when present in concentrations likely to be encountered in dealing with commercial grades of acetic acid; ethylidene diacetate, copper acetate, acetaldehyde (up to 1%) and water (up to 10%).

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THE MODIFIED LAMBERT CONFORMAL PROJECTION FOR POLAR AREAS[1]

By C. H. Ney[2]

Abstract

The search for a map suitable for aerial navigation over polar regions has led to the development of the Modified Lambert Conformal Projection for Polar Areas. In this paper the author points out the properties required in a map for polar navigation, and shows to what extent this projection satisfies these requirements.

Introduction

During the last war, the military importance of the Canadian Arctic was brought sharply into focus when it was found that a German meteorological station had been set up in Greenland to aid the Nazi Air Force in its attacks on the British Isles and to obtain information for possible attacks on the North American Continent. About the same time, the Allied Nations undertook the development of northern aerial routes linking Alaska and Northern Canada with Europe and Asia. As a result, it soon became apparent that the supply of maps of Arctic Canada suitable for aerial navigation was very limited and for the most part, unsatisfactory.

In 1945 and 1946, as a member of the Sub-committee on Navigation, Associate Committee on Aeronautical Research, National Research Council, the author undertook the development of a suitable polar projection for aerial navigation in Arctic Canada.

Most of the unsatisfactory features of long-range polar navigational maps had been well known for some time. Postwar experimental flights by the United States Army Air Force and the Royal Canadian Air Force from Continental Canada northward over the Arctic Archipelago have substantiated most of the known criticisms, which may be listed as follows:—

(*a*) Unsatisfactory basic map projections,
  (1) Where the meridians are delineated as curved lines, azimuths cannot readily be scaled from the map.
  (2) Lack of conformality.
  (3) Large distortion in scale at the outer edge of the map.

(*b*) Too small a scale.

(*c*) Congestion of meridians close to the Pole.

(*d*) Inadequate numbering of parallels of latitude and meridians. When the map is folded on the navigator's table, the numbering is often hidden from view.

(*e*) Congestion of isogonic lines near the geographic and magnetic poles.

(*f*) Inaccurate magnetic data.

(*g*) Inaccurate plotting of land masses.

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Contribution from the Triangulation Adjustments Division, Geodetic Survey of Canada, Mines, Forests and Scientific Services, Department of Mines and Resources, Ottawa, Canada.

[2] *Chief.*

Polar projections such as the stereographic, the equidistant, and the gnomonic give fairly satisfactory representations of terrestrial regions close to the Pole; but where the area to be mapped is extended down to latitude 65°, the selection of a suitable projection becomes a more difficult matter. For the investigator of polar mapping, there is a projection—the Lambert Conformal with two standard parallels- which merits consideration. This projection was first developed about 1770 by Johann Heinrich Lambert, a German mathematician, and was used extensively by the French in the First World War. In studying the mapping of polar areas, this projection might easily be passed over with scant consideration. However, a careful study of the subject leads to the conclusion that Lambert's projection may be so modified and adapted to high latitudes that it outclasses most of the other possible choices. Most of the standard projections are developed on a tangent plane or cylinder. The fact that the Lambert projection is developed on a secant cone suggests at once a considerable reduction in scale errors over the map as a whole. The conformal characteristics of the projection lend assurance that azimuths of great circle courses will be accurately shown.

On Lambert's projection, the scale errors around any point are the same in all directions. At each standard parallel, there is no error in scale. Elsewhere on the map, the magnitudes and signs of the scale errors vary with the latitude and depend to a large extent upon the spacing of the standard parallels. The scale errors are positive in sign for the areas between the southerly standard parallel and the outer edge of the map and between the northerly standard parallel and the Pole, and negative for the area between the two standard parallels. By taking advantage of this feature, a high degree of compensation may be attained in the distribution of scale errors over the map as a whole.

Modification of the Lambert Projection

In the true Lambert Conformal projection, $\theta = L.\Delta\lambda$, where θ is the mapping angle, $\Delta\lambda$ the corresponding true difference of longitude, and where the numerical value of L depends upon selected latitudes for the two standard parallels. As the value of L is always less than unity, the projection could not be used for mapping 360° in longitude at the Pole without leaving a wedge-shaped, blank area extending from the Pole to the outer edge of the map. Obviously this would be a very unsatisfactory type of map for aerial navigation.

By shifting the northerly standard parallel closer and closer to the Pole the value of L can be made to approach unity. At the same time, the critical position of the southerly standard parallel which will minimize and compensate the scale errors over the map as a whole can be found.

In order to place the standard parallels at the most advantageous positions to satisfy the requirements enumerated, a number of possible arrangements were tried out. A sufficient number of scale errors were computed for each

choice to be of help in making subsequent selections. After four or five trials, the following latitudes were adopted:

Northern Standard Parallel	89° 59′ 58″
Southern Standard Parallel	71° 00′ 00″

It was not possible to place the northerly standard parallel exactly at the Pole, as some of the formulae used in the computation of the map elements would then become indeterminate.

Resulting from this choice, the value of L was found to be 0.99737541—a close approximation to unity.

In the computation of the radii of the parallels of latitude and the scale errors, the value 0.99737541 was used throughout, in strict accordance with the mathematics of the true Lambert projection. In establishing the positions of the meridians, a slight deviation from the orthodox projection has been made. At a very slight sacrifice of conformality, the meridians have been established on the assumption that L equals unity. This means that the mapped value of the difference of longitude between two meridians is arbitrarily made equal to the true difference of longitude on the earth's surface. This modification, while altering the true Lambert projection very slightly with regard to conformality and scale, permits of 360° mapping around the Pole without leaving an undesirable gap extending from the Pole to the outer edge of the map.

The actual construction of the graticule is very simple. With the Pole as the center, concentric circles are drawn having radii equal to the calculated values. The meridians are then drawn as straight lines radiating from the Pole with the mapped differences of longitude equal to the corresponding values on the earth.

Scale of the Map

In conformity with the suggestions of a number of navigation officers of the R.C.A.F. and the U.S.A.A.F., a scale of 30 nautical miles to the inch has been adopted. A preliminary projection drawn on a scale of 60 nautical miles to the inch was tried out and found to be inadequate.

The Effect of Modification on the Scaled Distances

Fig. 1 shows the relation between the mapping angles θ and θ' on the true and modified projections, respectively.

The difference between the corresponding lengths of the great circle courses AB and AB' represents the distortion in scale due to modification. We then have

$$AB' - AB = 2\,R\cos\left(90^\circ - \frac{\Delta\lambda}{2}\right) - 2\,R\cos\left(90^\circ - \frac{L.\Delta\lambda}{2}\right)$$

$$= 2\,R\left(\sin\frac{\Delta\lambda}{2} - \sin\frac{L.\Delta\lambda}{2}\right).$$

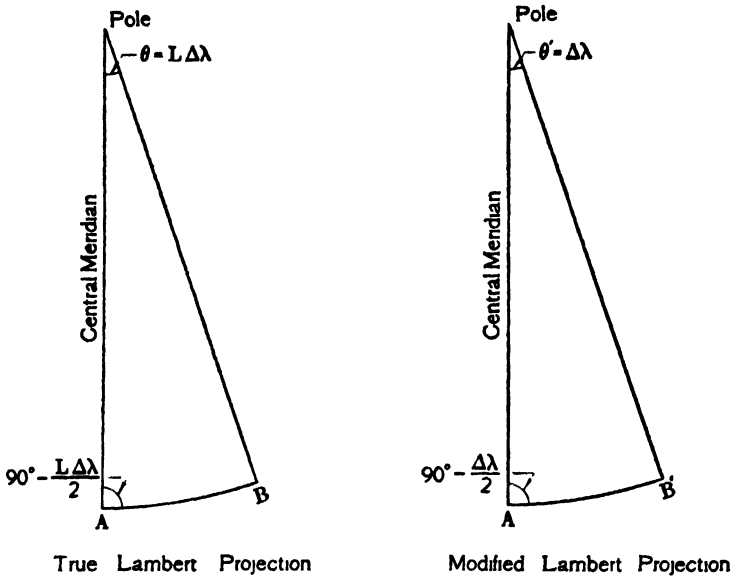

FIG. 1. *Mapping angle on the true and Modified Lambert projection.*

The ratio of distortion, due to modification, to course length, $\frac{AB' - AB}{AB}$, will be a maximum for a short east–west course. For such a course, $\Delta\lambda$ and $L.\Delta\lambda$ are so small that their values in radian measure may be substituted for their sines, so that

$$\frac{AB' - AB}{AB'} = 2\,R\frac{\left(\frac{\Delta\lambda}{2} - \frac{L.\Delta\lambda}{2}\right)}{R.\Delta\lambda}$$
$$= (1 - L)$$
$$= 0.0026.$$

This represents a ratio of distortion error to course length of about 3/10 of one per cent.

It is also found that if the point A remains stationary and the point B moves progressively around the latitude circle containing A, the ratio of error to course length will decrease progressively till a minimum value is reached when $\Delta\lambda = 180°$.

The Effect of Modification on the Scaled Azimuths

From Fig. 1 it is seen that on the true Lambert projection the azimuth at A of a course AB with both terminals on the same latitude circle is $90° - \frac{L.\Delta\lambda}{2}$, while the corresponding azimuth on the modified projection is $90° - \frac{\Delta\lambda}{2}$.

The error in azimuth at A, of the course AB, due to modification, therefore is $\frac{\Delta\lambda}{2}(1 - L)$ or $0.0013123\Delta\lambda$.

$$\begin{aligned} \text{For } \Delta\lambda &= 10°, \text{ error} = 1' \\ \Delta\lambda &= 90°, \quad \text{"} \quad = 7' \\ \Delta\lambda &= 180°, \quad \text{"} \quad = 14' \end{aligned}$$

As both the scale and azimuth errors resulting from modification are relatively small, they need not be considered a valid objection to the use of the modified projection for navigational or mapping purposes.

The Computation of the Map Elements

The formulae used in the computation of the various constants, the map elements, and the theoretical scale magnification are given below.

All computations are based on the Clarke Spheroid of 1866.

$$\begin{aligned} &\text{Semimajor axis } a = 6\ 378\ 206.4 \text{ meters} \\ &\text{Semiminor} \quad \text{"} \quad b = 6\ 356\ 583.8 \quad \text{"} \\ &\text{Eccentricity} \quad e = \sqrt{\frac{a^2 - b^2}{a^2}} \\ &\log e^2 = 7.8305026 - 10 \\ &\log \frac{b^2}{a^2} = 9.9970504 - 10 \end{aligned}$$

To Find Log tan $\frac{Z}{2}$, where Z is the isometric colatitude, we have

$$Z = 90 - \phi', \text{ and}$$

and

$$\operatorname{Tan} \phi' = \frac{b^2}{a^2} \tan \phi$$

where ϕ' and ϕ are the geocentric and geodetic latitudes, respectively.
For latitude 71°,

$$\frac{Z}{2} = 9°\ 33'\ 36''.20$$

$$\log \tan \frac{Z}{2} = 9.22639448 - 10$$

Similarly for latitude 89° 59′ 58″,

$$\log \tan \frac{Z}{2} = 4.68860440 - 10$$

To Find The Constant A

$$A = \frac{(1 - e^2 \sin^2 \phi)^{\frac{1}{2}}}{a \sin 1''}.$$

Substituting and reducing, we get

$$\log A_{(\phi = 71°)} = 8.50840856 - 10$$
$$\log A_{(\phi = 89°59'58'')} = 8.50825180 - 10.$$

To Find The Constant L

$$L = \frac{\log \cos \phi_1 - \log \cos \phi_2 - \log A_1 + \log A_2}{\log \tan \frac{Z_1}{2} - \log \tan \frac{Z_2}{2}},$$

where ϕ_1, A_1 and Z_1 pertain to latitude 71° and ϕ_2, A_2 and Z_2 pertain to latitude 89° 59′ 58″. Inserting the numerical values of the above symbols and reducing, we get

$$L = 0.99737541$$
$$\log L = 9.99885866 - 10.$$

To Find The Constant K

$$K = \frac{\cos \phi_1}{A_1 \sin 1'' \, L \tan^L \frac{Z_1}{2}} = \frac{\cos \phi_2}{A_2 \sin 1'' \, L \tan^L \frac{Z_2}{2}}.$$

For latitude 71°, the southerly standard parallel, we have

$$\begin{aligned}
\log A_1 &= 8.5084085 - 10 \\
\log \sin 1'' &= 4.6855749 - 10 \\
\log L &= 9.9988587 - 10 \\
\log \tan^L \frac{Z_1}{2} &= \frac{9.2284249 - 10}{2.4212669 - 10} \\
\log \cos \phi_1 &= 9.5126419 - 10 \\
\log K &= 7.0913750
\end{aligned}$$

A similar computation for latitude 89° 59′ 58″, the latitude of the northerly standard parallel, gives the same value of log K.

With the constants L and K evaluated, the radii of the concentric latitude circles for each degree of latitude between 65° and the Pole are computed from the formula

$$R = K \tan^L \frac{Z}{2}.$$

The resulting values are given in Table I.

The Scale Error

For the modified projection, the scale error at any parallel of latitude will be the algebraic sum of the theoretical scale error of the true Lambert projection and the scale error due to modification. As the latter has already been shown to have little practical significance, the theoretical value may be considered applicable to the modified projection. Its value is derived from the formula

TABLE I

Latitude	R, meters	R, inches*	Percentage scale error	Latitude	R, meters	R, inches*	Percentage scale error
65	2,763,834	49 713	1 98	78	1,313,528	23 627	− 1 53
66	2,650,330	47 672	1 61	79	1,203 668	21 650	− 1 68
67	2,537,225	45 637	1 25	80	1,093,958	19 677	− 1 81
68	2,424,191	43 610	0 91	81	984,378	17 706	− 1 93
69	2,312,108	41 588	0 60	82	874,911	15 737	− 2 03
70	2,200,063	39 573	0 29	83	765,536	13 770	− 2 10
71	2,088,333	37 563	0 00	84	656,232	11 804	− 2 16
72	1,976,901	35 559	− 0 27	85	546,975	9 838	− 2 19
73	1,865,747	33 559	− 0 62	86	437,741	7 874	− 2 20
74	1,754,855	31 565	− 0 76	87	328,198	5 909	− 2 18
75	1,644,205	29 574	− 0 98	88	219,205	3 943	− 2 11
76	1,533,778	27 588	− 1 18	89	109,794	1 975	− 1 96
77	1,423,562	25 606	− 1 36	90	0	0 000	0 00

Applicable to map on scale of 30 nautical miles to the inch

$$m = \frac{LRA \sin 1''}{\cos \phi},$$

where m is the magnification of the scale along any parallel of latitude. The percentage ratio of scale error to length of course therefore is $100\,(1 - m)$.

For latitude 71°,

$$\begin{aligned}
\log L &= 9\ 998\ 858\ 66 - 10 \\
{}'' \quad R &= 6\ 319\ 799\ 82 \\
{}'' \quad A &= 8\ 508\ 408\ 56 - 10 \\
\log \sin 1'' &= \underline{4\ 685\ 574\ 87 - 10} \\
&\ 9\ 512\ 641\ 91 - 10 \\
\log \cos 71^\circ &= 9\ 512\ 641\ 91 - 10 \\
{}'' \quad m &= 0 \\
m &= 1 \\
\text{Scale error} &= 0
\end{aligned}$$

At latitude 71°, the location of the southerly standard parallel, the scale error should of course be equal to zero.

For latitude 84°,

$$\begin{aligned}
\log L &= 9\ 998\ 858\ 66 - 10 \\
{}'' \quad R &= 5\ 817\ 057\ 28 \\
{}'' \quad A &= 8\ 508\ 267\ 94 - 10 \\
\log \sin 1'' &= \underline{4\ 685\ 574\ 87 - 10} \\
&\ 9\ 009\ 758\ 75 - 10 \\
\log \cos 84^\circ &= \underline{9\ 019\ 234\ 57 - 10} \\
{}'' \quad m &= 9\ 990\ 524 \quad - 10 \\
m &= 0\ 9784 \\
\text{Scale error} &= 2\ 16\%
\end{aligned}$$

Table I gives the radii of the latitude circles in meters and in inches for a map scale of 30 nautical miles to the inch. In addition, the theoretical scale errors on a true Lambert projection are given in column three for each degree of latitude between 65° and the North Pole.

Table II gives the values of log A.

TABLE II

Latitude	Log A, meters	Latitude	Log A, meters	Latitude	Log A, meters
65	8 5085159 − 10	74	8 5083643	83	8 5082738
66	8 5084964	75	8 5083509	84	8 5082680
67	8 5084776	76	8 5083384	85	8.5082631
68	8 5084594	77	8 5083267	86	8 5082590
69	8 5084418	78	8 5083158	87	8 5082559
70	8 5084248	79	8 5083056	88	8 5082536
71	8 5084086	80	8 5082964	89	8 5082523 − 10
72	8 5083930	81	8 5082880		
73	8 5083783	82	8 5082805		

From the tabulation, it is seen that the error at the outer edge of the map is +1.98%, at latitude 71° and at the North Pole it is zero, and at latitude 86° it is − 2.20%. Owing to the compensating effect of the positive and negative signs of the errors at different parts of the map, the over-all scaled value of a long course is usually correct to within 1%.

Examples of Great-Circle Courses Plotted on the Modified Lambert Projection

To demonstrate the accuracy with which azimuths and distances may be scaled from the projection, a number of long geodetic lines* joining assumed terminal points on the earth's surface were plotted on a Modified Lambert Projection. To facilitate the demonstration, the latitudes and longitudes of a number of intermediate points on each course were computed by precise geodetic formulae. The initial azimuths and the azimuths† of the courses at each intermediate station, and the distances between intermediate points, were also computed so that the scaled values could be accurately compared.

Table III gives the latitudes and longitudes of the intermediate points on each course. It also gives the theoretical and scaled azimuths of the geodetic line at each point on the course and the differences between the theoretical and scaled values. It will be noted that, for the chosen lines, the maximum error in the scaled azimuth at any point was about one-third of a degree.

* *A geodetic line is the shortest line joining two points on the earth's surface treated as an ellipsoid of revolution.*

Aerial navigators usually consider their flight lines as great-circle courses on a sphere having a radius equal to the mean radius of the earth. Azimuths and lengths of the courses computed on this assumption, while not strictly correct, are usually well within the limits of accuracy required for aerial navigation.

† *In Canadian survey practice, azimuths are reckoned clockwise from the north from 0° to 360°.*

TABLE III

COMPARISON OF AZIMUTHS (GREAT CIRCLE COURSE)

Point	Latitude	Longitude	Azimuth		Difference
			Computed	Scaled	
Course A — *From Point 1* {*Lat.* 65° N. *Long.* 145°59′ 42″.4 W. *to Point 7* {*Lat.* 80° N. *Long.* 10°21′ 36″.4 E. *Length* = 2071.1 *nautical miles*					
1	65° N.	145° 59′ 42″ 4 W.	7° 05′ 13″ 6	7° 15′	10′
2	68° N.	145° 00′ 00″ 0 W.	8° 00′ 00″ 0	7° 55′	5′
3	74° N.	141° 56′ 12″ 2 W.	10° 54′ 01″ 5	10° 40′	14′
4	80° N.	135° 12′ 32″ 9 W.	17° 27′ 53″ 9	17° 30′	2′
5	87° N.	67° 44′ 57″ 0 W.	84° 40′ 57″ 1	84° 30′	11′
6	87° N.	57° 05′ 59″ 5 W.	95° 19′ 02″ 6	95° 15′	4′
7	80° N.	10° 21′ 36″ 4 E.	162° 32′ 06″ 3	162° 30′	2′
Course B — *From Point 1* {*Lat.* 65° N. *Long.* 129°01′ 12″ 6 W. *to Point 5* {*Lat.* 79° N. *Long.* 51°51′ 18″ 4 W. *Length* = 1495.7 *nautical miles*					
1	65° N.	129° 01′ 12″ 6 W.	26° 18′ 42″ 3	26° 30′	11′
2	68° N.	125° 00′ 00″ 0 W.	30° 00′ 00″ 0	29° 45′	15′
3	74° N.	111° 29′ 33″ 4 W.	42° 47′ 42″ 5	42° 45′	3′
4	79° N.	74° 28′ 01″ 0 W.	78° 53′ 46″ 3	79° 10′	16′
5	79° N.	51° 51′ 18″ 4 W.	101° 06′ 13″ 7	100° 55′	11′
Course C — *From Point 1* {*Lat.* 65° N. *Long.* 100° W. *to Point 4* {*Lat.* 73° N. *Long.* 61° 27′ 21″ 6 W. *Length* = 937.2 *nautical miles*					
1	65° N.	100° 00′ 00″ 0 W.	42° 47′ 47″ 0	42° 40′	8′
2	68° N.	92° 07′ 04″ 4 W.	50° 01′ 44″ 6	50° 00′	2′
3	71° N.	79° 30′ 36″ 2 W.	61° 50′ 54″ 0	61° 50′	1′
4	73° N.	61° 27′ 21″ 6 W.	79° 02′ 05″ 3	78° 50′	12′
Course D — *From Point 1* {*Lat.* 65° N. *Long.* 96°04′ 20″ W. *to Point 3* {*Lat.* 70° N. *Long.* 71°49′ 23″ 8 W. *Length* = 628.8 *nautical miles*					
1	65° N.	96° 04′ 20″ 0 W.	50° 50′ 15″ 4	50° 30′	20′
2	68° N.	85° 00′ 00″ 0 W.	61° 00′ 00″ 0	61° 10′	10′
3	70° N.	71° 49′ 23″ 8 W.	73° 18′ 37″ 2	73° 35′	16′
Course E — *From Point 1* {*Lat.* 65° N. *Long.* 88° 16′ 40″ W. *to Point 3* {*Lat.* 68° N. *Long.* 65° 00′ 00″ 0 W. *Length* = 583.4 *nautical miles*					
1	65° N.	88° 16′ 40″ 0 W.	61° 38′ 23″ 1	61° 25′	13′
2	67° N.	76° 48′ 44″ 4 W.	72° 07′ 16″ 7	72° 10′	3′
3	68° N.	65° 00′ 00″ 0 W.	83° 02′ 26″ 0	83° 15′	13′

TABLE III (continued)

COMPARISON OF AZIMUTHS (GREAT CIRCLE COURSE)

Point	Latitude	Longitude	Azimuth		Difference
			Computed	Scaled	
Course F					
From Point 1 {*Lat.* 65° N. *Long.* 120° W. *to Point 9* {*Lat.* 75° 15′ N. *Long.* 45° 51′ 25″.0 W. *Length* = 1509.8 *nautical miles*					
1	65°	120° 00′ 00″ 0 W.	35° 20′ 00″ 0	35° 15′	5′
2	67°	116° 17′ 48″ 8 W.	38° 13′ 01″ 2	38° 25′	18′
3	69°	111° 11′ 12″ 0 W.	42° 59′ 33″ 0	43° 00′	0′
4	71°	105° 10′ 51″ 0 W.	48° 38′ 15″ 3	48° 10′	2′
5	73°	97° 13′ 03″ 0 W.	56° 41′ 21″ 5	56° 10′	1′
6	71° 30′	87° 25′ 02″ 4 W.	66° 06′ 01″ 9	66° 15′	9′
7	75° 30′	75° 45′ 27″ 6 W.	77° 21′ 57″ 2	77° 10′	12′
8	75° 51′ 31″.1	62° 43′ 18″ 8 W.	90° 00′ 00″ 0	90° 10′	10′
9	75° 15′	45° 51′ 25″ 0 W.	106° 20′ 21″ 5	106° 35′	15′

Table IV shows the theoretical and scaled distances, respectively, between the intermediate points on the lines. It also shows the difference between the two values expressed as a percentage of the scaled distance. It is seen that the maximum ratio error in a scaled distance is 2.2%.

Long great-circle courses will in general be slightly curved lines concave towards the pole. They diverge from the map chord, which is the straight line joining the terminal points of any course. Fig. 3 shows the divergence between the map chords and the great-circle courses for each of the six experimental flight lines *A*, *B*, *C*, *D*, *E* and *F*.

Nomogram for Plotting Great-Circle Courses

For laying down great-circle courses graphically on the projection with speed and accuracy, a nomogram shown in Fig. 2 has been developed. It gives at once the offset distance at the center of the map chord to the great-circle course and the angle in degrees at each terminal point between the map chord and the curved line constituting the great-circle course.

Points may also be established by offset from the chord at quarter-length intervals. This, however, should not be necessary except for extremely long courses.

The nomogram is applicable only to the full size map of Arctic Canada on a scale of 30 nautical miles to the inch. To be applicable to the linecut reproduction of the map shown in Fig. 3 (about one-fourteenth original scale), the numerical values of the chord length in inches and the perpendicular distance in inches on the nomogram scale shown in Fig. 2 would have to be similarly reduced.

TABLE IV

COMPARISON OF DISTANCES (NAUTICAL MILES)

Points	Distance: Computed	Distance: Scaled	Difference	Percentage error
Course A				
1–2	182.1	184.2	+ 2.1	+1.1
2–3	366.1	367.8	+ 1.7	+0.5
3–4	372.3	365.7	− 6.6	−1.8
4–5	558.7	546.0	− 12.7	−2.2
5–6	33.2	32.7	− 0.5	−1.5
6–7	558.7	545.9	− 12.8	−2.2
1–7	2071.1	2040.9*	− 30.2	−1.5
Course B				
1–2	204.6	207.3	+2.7	+1.3
2–3	415.8	417.0	+1.2	+0.3
3–4	586.9	578.1	−8.8	−1.5
4–5	258.4	255.0	−3.4	−1.3
1–5	1495.7	1486.8*	−8.9	−0.6
Course C				
1–2	261.2	266.1	+4.9	+1.9
2–3	320.5	322.2	+1.7	+0.5
3–4	355.5	354.0	−1.5	−0.4
1–4	937.2	942.0*	+4.8	+0.5
Course D				
1–2	320.7	325.3	+4.6	+1.4
2–3	308.1	310.8	+2.7	+0.9
1–3	628.8	636.1*	+7.3	+1.1
Course E				
1–2	305.0	309.3	+4.3	+1.4
2–3	278.4	280.8	+2.4	+0.9
1–3	583.4	590.1*	+6.7	+1.2
Course F				
1–2	150.7	153.3	+2.6	+1.7
2–3	159.0	160.5	+1.5	+0.9
3–4	172.5	173.1	+0.6	+0.3
4–5	198.0	198.3	+0.3	+0.2
5–6	188.0	186.9	−1.1	−0.6
6–7	191.2	189.3	−1.9	−1.0
7–8	195.1	193.2	−1.9	−1.0
8–9	255.3	255.6	+0.3	+0.1
1–9	1509.8	1506.6*	+3.2	+0.2

* *The scaled distance along the straight line joining the terminals is slightly less than the sum of the component parts of the great-circle course.*

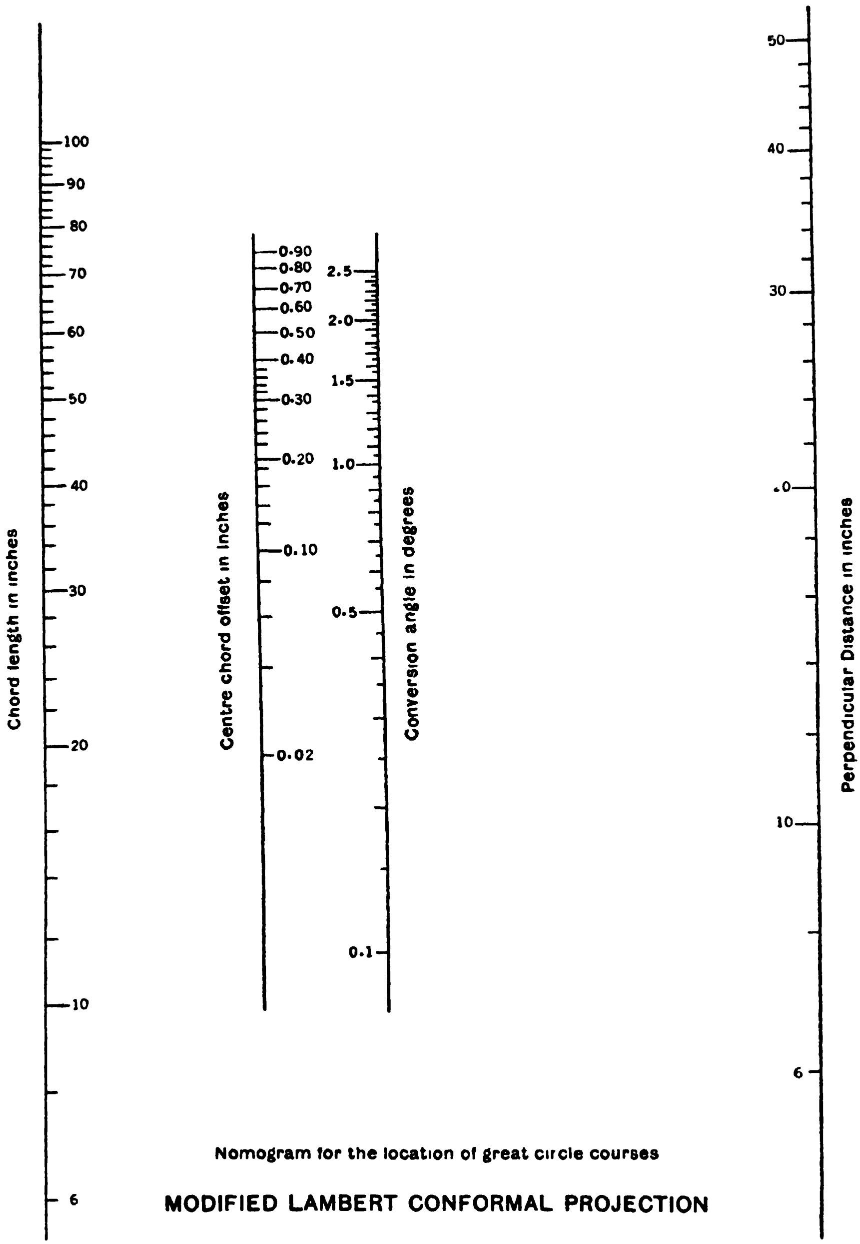

FIG. 2. *Nomogram.*

Directions for Using the Nomogram

(1) On the map, join the plotted terminal points of the course to be flown with a straight line to form the map chord.

(2) Measure the length of the map chord in inches.

(3) Measure the perpendicular distance from the geographical pole to the chord.

(4) Place a straight edge on the nomogram with one end on left-hand scale at the reading corresponding to the chord length and the other end on the right-hand scale at the reading corresponding to the perpendicular distance.

(5) At the point where the straight edge intersects the center-chord offset scale, read off the value of the offset distance from the center of the chord to the great-circle course. The latter will always be on the side of the chord remote from the pole.

(6) If more points are required on the great-circle course, join the newly established central point with each terminal, forming two new chords. The offset distance to the great-circle course from the center of each new chord will be one-quarter of the original offset distance.

(7) The initial azimuth of the great-circle course may be readily derived by adding (or subtracting) the value of the conversion angle between the chord and the great circle course. This angle may be taken directly from the nomogram by setting a straight edge at the corresponding reading of the chord length and perpendicular distance on the left and right-hand scale, respectively, and noting where the straight edge intersects the conversion angle scale. The conversion angle is added to the scaled azimuth of the chord for all azimuths between 0° and 180° and subtracted for all azimuths between 180° and 360°.

By laying off the conversion angles on the chart from the terminals of the chord, and establishing the central point on the great-circle course by offset distance from the map chord, the great-circle course may be drawn with sufficient accuracy for ordinary navigational purposes.

Numerical Example—Course F

Scaled chord length	= 50″.3
Scaled perpendicular distance	= 27″.6
From the nomogram, we get	
(*a*) Center chord offset	= 0″.36
(*b*) Conversion angles at points 1 and 9 between chord and great-circle course	= 1° 30′

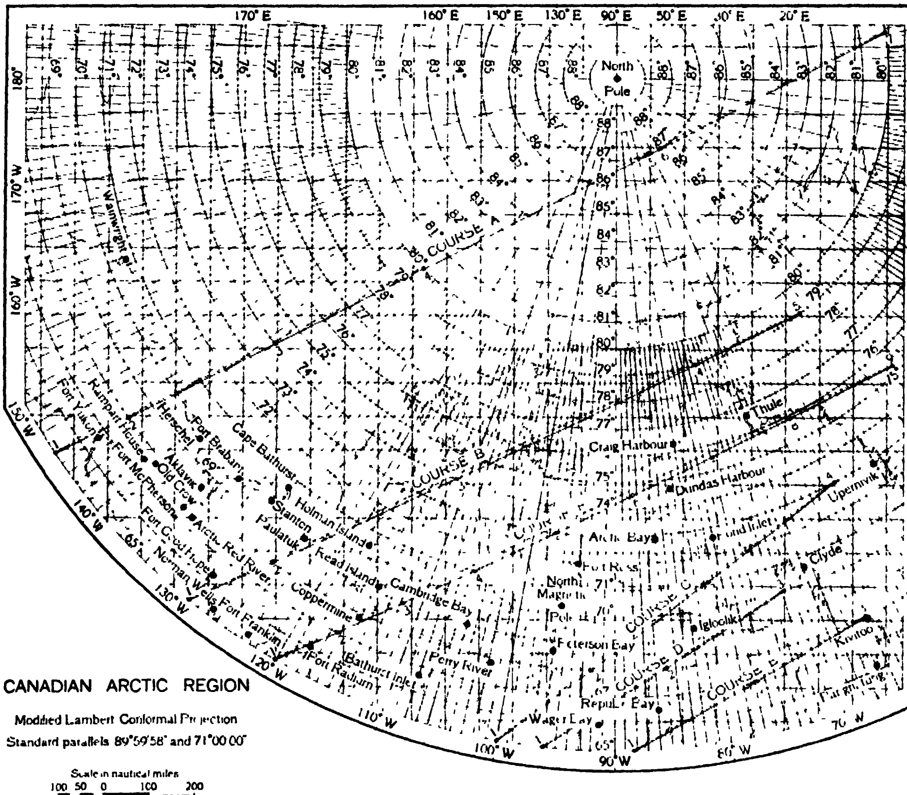

FIG. 3. *Reproduction of Map of Arctic Canada—on Modified Lambert conformal projection.*

Adding to (*b*) the scaled value of the initial azimuth of map chord (33° 45′), we get 35° 15′ as the initial azimuth of the great-circle course. The calculated initial azimuth is given in Table III as 35° 20′, differing only by 5′ from the value derived by the graphical method.

The value of the center chord offset for the map chord to the great-circle course scaled directly from the plotted position of Course *F* (by Table III) is 0″.37, giving an agreement to 1/100 in. with the value derived from the nomogram.

With the aid of a flexible ruler or baton, the two terminal points and the center point of the great-circle course may be joined by a curved line giving an almost exact representation of the true great-circle course.

General Description of the Map

Fig. 3 shows a reproduction of the finished map, upon which the six great-circle courses have been plotted. The spacing and numbering* of meridians and latitude circles, the faint delineation of land masses and topographical

**On the small-scale reproduction of the map shown in Fig. 3, it was not possible to show all the numbering of meridians and parallels of latitude.*

features, and the marking of settlements and air bases are, in nearly all cases, in conformity with suggestions put forward by officers of the United States Army Air Force and the Royal Canadian Air Force. The square grid system with lines parallel to and at right angles to the Greenwich Meridian was included to facilitate navigation by the "*G*" system first proposed by W/C K. C. Maclure of the R.C.A.F., who flew over the North Pole in the Aries in 1945.

Airmen who have made extensive use of this map on flights over polar and subpolar areas have reported the following desirable features:

(*a*) The limits of the projection extend from latitude 65° N. to 2° beyond the pole.

(*b*) With the standard parallels at latitude 89° 59′ 58″ and 71° 00′ 00″, the scale errors over the map as a whole are practically negligible.

(*c*) The azimuths or true bearings of great-circle courses may be scaled with sufficient accuracy from the chart.

(*d*) The scale of 30 nautical miles to the inch is satisfactory.

(*e*) The omission of isogonals until such time as more reliable magnetic data are available.

(*f*) The prominence of latitude and longitude designations.

(*g*) The decreasing number of meridians in the polar region lessens congestion.

(*h*) The grid lines are conveniently spaced.

The navigational map of Arctic Canada has, however, one undesirable feature common to all maps of our subpolar areas. As the systematic mapping of areas north of latitude 65° has been inaugurated in recent years only, there are insufficient survey data available at the present time to make possible the correct delineation of the polar land masses and details of topography. At the completion of several years of the present mapping program, this condition should no longer obtain.

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CONTRAFLOW CONTRAROTATING TURBOCOMPRESSORS[1]

DONALD L. MORDELL[2]

Abstract

The performance of a turbocompressor comprised of a large number of mechanically independent compressor and turbine stages is considered. Examination of the equilibrium conditions of any stage shows its performance, for a given design, to be dependent on four variables and hence the performance of the complete unit is also dependent on the same four variables. Exact arithmetical calculation would be possible, but very tedious. In order to render computation easier, the conception of reflected conditions is introduced. Physically this implies independence of each stage, in some respects, from its neighbors. The assumption is likely to be in error least for intermediate stages, and most for the first and last stages. Methods of expressing the aerodynamic performance of the blades of the compressor and turbine stages are introduced to render calculation easier. Some calculated performance figures are compared with experimental values and show by their reasonable agreement that the assumptions used are valid The methods can be applied to other types of complex turbocompressor units by suitable modification of procedure and details.

Introduction

In 1929, A. A. Griffith put forward proposals for the use of the internal combustion turbine for aircraft propulsion (1). He showed that with the then existing knowledge such an engine was a practical proposition, and he also investigated mathematically the best arrangement of engine. A gas turbine engine consists essentially of an air compressor, combustion chamber, turbine to drive the compressor, and turbine to supply the useful output. Note that the two turbines may in fact form a single unit, and that in the common jet propulsion engine the second turbine is replaced by a propulsive jet. Griffith proved that in order to obtain a wide range of efficient operation it was desirable to arrange the compressor, and the turbine driving it, in a series of mechanically independent stages, each small compressor stage being driven by its own small turbine stage. The use of 'small' here denotes a stage over which the pressure ratio is small. The mechanical arrangement of such a unit is shown diagrammatically in Fig. 1.

In this paper we discuss some aspects of the performance of such a unit, known as a contraflow compressor. The problem may be put as follows. Suppose we have such a unit of given geometrical design. We can express its

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[2] *Associate Professor of Mechanical Engineering.*

over-all performance in various terms, for example, the mass flow, and initial density of the air entering the compressor, and its compression ratio and efficiency, and the four corresponding factors for the turbine. We shall show that in fact there are but four independent variables, and they may be conveniently

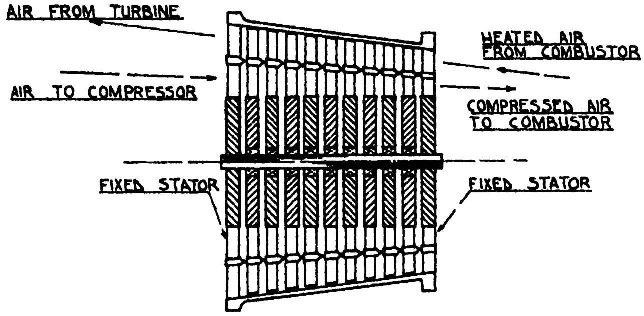

FIG. 1. *Diagram of a contraflow turbocompressor.*

taken as the mass flow and initial density of the air at the compressor inlet and at the turbine inlet. The problem then is to calculate from these four independent variables the values of the other four variables and also, the working conditions of any of the, possibly many, compressor or turbine stages.

Nomenclature

M — mass flow, pounds per second,
A — annulus area, square feet,
P — total pressure, poundals per square foot,
p — static pressure, poundals " " ",
T — total temperature, °K.,
t — static temperature, °K.,
ρ — density, pounds per cubic foot,
u — peripheral velocity of blade, feet per second,
v — gas velocity,
v_a — gas axial velocity,
v_w — gas whirl velocity,
ϕ — u/v_a,
r — mean blade radius,
α — angle between vector representing a gas velocity relative to a blade and the axial direction,
β — angle between vector representing a gas velocity relative to the frame of the machine and the axial direction,
Suffix 1 indicates condition at entry to a stage,
2 indicates condition at exit from a stage,
Prefix c indicates a compressor stage,
t indicates a turbine stage,
n denotes conditions at stage number n.

The stages are numbered from the H.P. end, i.e., the entry to the turbine and the exit from the compressor.

E.g., ${}_{nt}X_2$ indicates the value of quality X at exit from the n^{th} turbine stage.

A bar over a quality denotes the value of the ratio.

E.g., $\overline{X} = \dfrac{{}_cX}{{}_tX}$.

General Theory

We start by considering the most general case. The assumptions we make are, that at any stage, we may typify air conditions over the annulus by referring to conditions at the mean radius, and that in any stage there is negligible

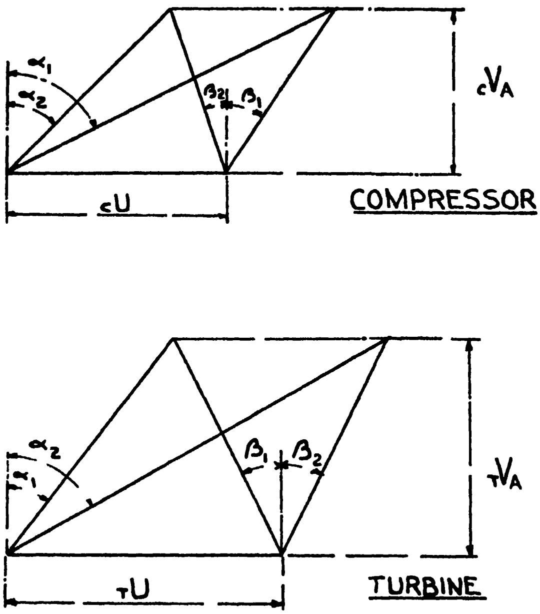

FIG. 2. *Contraflow compressor—typical velocity vector triangles*

change in the axial velocity. This does not preclude a change over the whole compressor or turbine, but merely that such changes may be represented by small discontinuities between stages.

In Fig. 2 we show diagrams representing the velocity vectors for any compressor stage and for any turbine stage. Then in any compressor stage n, the work done per pound per second of air flowing is, by Euler's momentum theory

$$ {}_{nc}u \cdot {}_{nc}\Delta v_\omega = {}_{nc}u \cdot {}_{nc}v_a \left[\tan {}_{nc}\alpha_1 - \tan {}_{nc}\alpha_2\right], $$

where Δv_ω is the change of whirl velocity.

But $$\tan {}_{nc}\alpha_1 = \frac{{}_{nc}u}{{}_{nc}v_a} + \tan {}_{nc}\beta_1 = {}_{nc}\phi + \tan {}_{nc}\beta_1,$$

and $$\tan {}_{nc}\beta_1 = \tan {}_{(n+1)c}\beta_2 = {}_{(n+1)c}\phi - \tan {}_{(n+1)c}\alpha_2.$$

So the work done per pound per second =

$$ {}_{nc}v^2{}_{a}\cdot{}_{nc}\phi\,[{}_{nc}\phi + {}_{(n+1)c}\phi - \tan{}_{nc}\alpha_2 - \tan{}_{(n+1)c}\alpha_2]\,. \tag{1} $$

Similarly in any turbine stage n, the work done per pound of gas per second is

$$ {}_{nt}v_a{}^2\cdot{}_{nt}\phi[\tan{}_{nt}\alpha_2 - \tan{}_{nt}\alpha_1]\,. $$

But

$$ \tan{}_{nt}\alpha_1 = {}_{nt}\phi - \tan{}_{nt}\beta_1 $$

and

$$ \tan{}_{nt}\beta_1 = \tan{}_{(n-1)t}\beta_2 = \tan{}_{(n-1)t}\alpha_2 - {}_{(n-1)t}\phi. $$

So the work done per pound-second =

$$ {}_{nt}v^2{}_{a}\cdot{}_{nt}\phi[\tan{}_{(n-1)t}\alpha_2 + \tan{}_{nt}\alpha_2 - {}_{(n-1)t}\phi - {}_{nt}\phi]\,. \tag{2} $$

For the rotor to be in equilibrium, the total work done by the turbine stage must equal that absorbed by the compressor, plus any frictional or windage loss. We may write the equilibrium condition as

$$ {}_cM\cdot{}_{nc}v^2{}_{a}\cdot{}_{nc}\phi[{}_{nc}\phi + {}_{(n+1)c}\phi - \tan{}_{nc}\alpha_2 - \tan{}_{(n+1)c}\alpha_2] = $$
$$ k\cdot{}_tM\cdot{}_{nt}v^2{}_{a}\cdot{}_{nt}\phi[\tan{}_{(n-1)t}\alpha_2 + \tan{}_{nt}\alpha_2 - {}_{(n-1)t}\phi - {}_{nt}\phi]. \tag{3} $$

Where ${}_cM$ and ${}_tM$ are the compressor and turbine mass flows and k is a factor nearly equal to 1, representing friction and windage losses.

Rearranging Equation (3) we have

$$ \frac{\bar{M}\cdot{}_n\bar{v}_a{}^2\cdot{}_n\phi}{k}\cdot[{}_{nc}\phi + {}_{(n+1)c}\phi - \tan{}_{nc}\alpha_2 - \tan{}_{(n+1)c}\alpha_2] = $$
$$ [\tan{}_{(n-1)t}\alpha_2 + \tan{}_{nt}\alpha_2 - {}_{(n-1)t}\phi - {}_{nt}\phi] $$

or

$$ {}_{(n-1)c}\phi\left[\frac{1}{{}_{(n-1)}\phi}\right] + {}_{nc}\phi\left[\frac{\bar{M}\cdot{}_n\bar{v}_a{}^2\cdot{}_n\bar{\phi}}{k} + \frac{1}{{}_n\bar{\phi}}\right] + {}_{(n+1)c}\phi\left[\frac{\bar{M}\cdot{}_n\bar{v}_a{}^2\cdot{}_n\phi}{k}\right] = $$
$$ [\tan{}_{nc}\alpha_2 + \tan{}_{(n+1)c}\alpha_2]\cdot\frac{\bar{M}\cdot{}_n\bar{v}_a{}^2\cdot{}_n\phi}{k} + [\tan{}_{(n-1)t}\alpha_2 + \tan{}_{nt}\alpha_2]\,. \tag{4} $$

This equation is the general equation relating the speed of any rotor to the speeds of rotors on either side, and can be used for any rotor. It is a second order difference equation and in its general solution has two arbitrary constants. It is evident that these two constants are related to the direction of the air before entering the compressor and the turbine, i.e., the effect of any stationary guide vanes. To solve Equation (4) as it stands, is very tedious, and for the purposes of this analysis, we can make certain simplifying assumptions, the validity of which will be discussed later.

Let us suppose

$$ \begin{aligned} {}_n\bar{v}_a &= v_a && \text{for all } n, \\ {}_n\phi &= \bar{\phi} && \text{for all } n, \\ {}_{nc}\alpha_2 &= c && \text{for } 1 \leq n \leq N, \\ {}_{nt}\alpha_2 &= t && \text{for } 1 \leq n \leq N. \end{aligned} $$

Note that since $\bar{\phi} = \bar{u}/\bar{v}_a = r/\bar{v}_a$ then $\bar{v}_a{}^2\bar{\phi} = \bar{r}\,\bar{v}_a$.

Equation (4) then becomes

$$ {}_{(n-1)c}\phi \cdot \frac{\bar{v}_a}{r} + {}_{nc}\phi\left[\frac{\bar{M}\bar{v}_a\bar{r}}{k} + \frac{v_a}{\bar{r}}\right] + {}_{(n+1)c}\phi\left[\frac{\bar{M}\bar{v}_a\bar{r}}{k}\right] = \frac{\bar{M}\bar{v}_a\bar{r}}{k} \times 2c + 2t. $$

For further convenience put $\dfrac{\bar{M}\bar{v}_a\bar{r}}{k} = k_1$, $\dfrac{\bar{v}_a}{r} = k_2$

then
$$ {}_{(n-1)c}\phi \cdot k_2 + {}_{nc}\phi[k_1 + k_2] + {}_{(n+1)c}\phi \cdot k_1 = k_1 . 2c + 2t. \tag{5} $$

Put
$$ {}_{nc}\phi = Ax^n + \frac{k_1 . 2c + 2t}{2[k_1 + k_2]}. $$

Then substituting in Equation (5) we have

$$ Ax^{n-1}[k_2 + (k_1 + k_2)x + k_1x^2] = 0. $$

So either $Ax^{n-1} = 0$ which means that ${}_{nc}\phi$ is constant for all n, irrespective of any boundary conditions, which is obviously absurd, or else

$$ k_1x^2 + (k_1 + k_2)x + k_2 = 0 $$
$$ x^2 + (1 + k_2/k_1)x + k_2/k_1 = 0. $$

The roots of this equation are $x_1 = -1$, $x_2 = -\dfrac{k_2}{k_1}$.

So the general solution of Equation (5) becomes

$$ {}_{nc}\phi = A[-k_2/k_1]^n + B[-1]^n + \frac{k_1 . 2c + 2t}{2(k_1 + k_2)}. \tag{6} $$

It remains to determine A and B. We do this by considering rotor $n = 1$, and rotor $n = N$. At $n = 1$, i.e., the first turbine stage, the direction of the air, relative to the frame of the machine, is given by $\tan^{-1}\beta_t$, say.

Then Equation (5) becomes

$$ {}_{1c}\phi[k_1 + k_2] + {}_{2c}\phi \cdot k_1 = k_1 . 2c + t + \beta_t. \tag{7} $$

At $n = N$, if the direction of the air, entering the compressor, relative to the frame of the machine is given by $\tan^{-1}\beta_c$, then we have

$$ {}_{(n-1)c}\phi \cdot k_2 + {}_{nc}\phi(k_1 + k_2) = (c - \beta_c)k_1 + 2t. \tag{8} $$

Substitution of Equation (6) in Equations (7) and (8) yields

$$ (k_1 + k_2)\left[-\frac{k_2}{k_1} \cdot A - B + \frac{k_1 . 2c + 2t}{2(k_1 + k_2)}\right] + k_1\left[\left(\frac{k_2}{k_1}\right)^2 A + B + \frac{k_1 . 2c + 2t}{2(k_1 + k_2)}\right] $$
$$ = k_1 2c + t + \beta_t $$

$$ k_2\left[A\left(-\frac{k_2}{k_1}\right)^{N-1} + B(-1)^{N-1} + \frac{k_1 . 2c + 2t}{2(k_1 + k_2)}\right] $$
$$ + (k_1 + k_2)\left[A\left(-\frac{k_2}{k_1}\right)^N + \beta(-1)^N + \frac{k_1 . 2c + 2t}{2(k_1 + k_2)}\right] = (c - \beta_c)k_1 + 2t. $$

Solving for A and B, and noting that, for an aircraft engine, N would desirably be even, so as to balance gyroscopic loadings, we have

$$A = \frac{\dfrac{2k_1c + k_1\beta_c + t}{k_1} - \dfrac{k_12c + t + \beta_t}{k_2}}{1 + (k_2/k_1)^N(2 + k_2/k_1)}$$

$$B = \frac{t - k_2c - \beta_t(1 + k_2/k_1)}{k_2(1 + k_2/k_1)} - A\,.$$

These then are the two arbitrary constants to go in Equation (6). We note that Equation (6) gives us ${}_{nc}\phi$ as a function of

n,	the stage position and N the total number of stages,
c, t,	the gas leaving angles from the moving blades,
β_c, β_t,	the gas entry angle to the compressor and turbine,
k_1, k_2, i.e.,	$\dfrac{\bar{M}\bar{v}_a\bar{r}}{k}$ and $\dfrac{v_a}{\bar{r}}$.

If we consider a given machine, c, t, β_c, β_t, r, and k are all fixed. If now we specify $\bar{M}_a$ and $\bar{v}_a$, or what is the same, $\bar{M}$ and $\bar{\rho}$ since $\bar{v}_a = \bar{M}/\bar{\rho}A$ Equation (6) is completely defined, and the value of ${}_c\phi$, and thence ${}_t\phi$ can be calculated for each stage of the compressor and turbine. Now for any given value of ${}_cM$ and the density at entry to the compressor, we can calculate ${}_{Nc}v_a$, and since we know ${}_{Nc}\phi$, ${}_{Nc}u$ is known. Once the blade velocity and axial flow velocity are known, the performance of the stage is completely fixed. Thus the conditions leaving the stage can be calculated and the next stage considered, and so on. In short, if we know the four independent variables $\bar{M}$, $\bar{\rho}$, and ${}_cM$, ${}_c\rho$ the performance of the whole unit is completely specified. There is no loss of generality in the simplifying assumptions made and this conclusion applies to any machine of this type.

Reflected Conditions

It is evident that detailed calculations are tedious, and, in any event, the blade angles in any real compressor will not be equal for all compressor stages, so that the mathematical expression for the parameter ${}_{cn}\phi$ becomes most complicated. Fortunately a simpler method can be used for most cases, without introducing errors greater than those implicit in necessarily assumed data concerning blade performance, to which we will refer later.

When ${}_{nc}\beta_1 = {}_{nc}\beta_2$, and ${}_{nt}\beta_1 = {}_{nt}\beta_2$, we have a symmetrical or reflected variation of the absolute velocity of the gas in its passage through the machine, which can be regarded as the condition to be aimed at in design. If we assume that this condition is satisfied, the mathematics simplifies considerably. Physically, we are in effect considering each rotor on its own without influence being exerted on it by its neighbors. The justification for this rather drastic assumption is that it makes the sum practicable, and experience shows that the results given are sufficiently near the truth to be of great use.

Referring to the vector triangles of Fig. 2, it is evident that if we suppose $\beta_1 = \beta_2$ in both cases, then the change of tangential velocity component can be written

$$_c\Delta v_\omega = 2(_cu - {_cv_a} \tan {_c\alpha_2})$$
$$_t\Delta v_\omega = 2(_cv_a \tan {_t\alpha_2} - {_tu}) .$$

Expressing the equilibrium of the rotor, we have

$$_cM.{_cu}.2(_cu - {_cv_a} \tan {_c\alpha_2}) = k.{_tM}{_tu}\, 2(_tv_a \tan {_t\alpha_2} - {_tu})$$
$$_cM.2\, {_c\phi}{_cv_a}^2(_c\phi - \tan {_c\alpha_2}) = k.{_tM}\, 2{_t\phi}{_tv_a}^2(\tan {_t\alpha_2} - {_t\phi})$$
$$\frac{\bar{M}\phi\bar{v}_a^2}{k}(_c\phi - \tan {_c\alpha_2}) = \tan {_t\alpha_2} - \frac{_c\phi}{\phi},$$

or

$$_c\phi = \frac{\dfrac{\bar{M}\phi v_a^2}{k} . \tan {_c\alpha_2} + \tan {_t\alpha_2}}{\dfrac{\bar{M}\bar{\phi}\bar{v}_a^2}{k} + \dfrac{1}{\phi}} .$$

Remembering that $\bar{\phi} = \bar{u}/\bar{v}_a = \bar{r}/\bar{v}_a$

and $\bar{v}_a = \bar{M}/\bar{\rho}\bar{A}$,

we have

$$_c\phi = \frac{\dfrac{\bar{M}^2\bar{r}}{k\bar{A}\bar{\rho}} \tan {_c\alpha_2} + \tan {_t\alpha_2}}{\dfrac{\bar{M}^2\bar{r}}{k\bar{A}\rho} + \dfrac{\bar{M}}{\bar{r}\bar{A}\bar{\rho}}} . \tag{9}$$

Hence for any given stage $_c\phi$ is a function of $\bar{M}$ and $\bar{\rho}$, just as we found in the more general case, Equation (6) Also since $_t\phi = \dfrac{\bar{M}}{\bar{\rho}\bar{A}\bar{r}} . {_c\phi}$

$$_t\phi = \frac{\tan {_t\alpha_2} + \dfrac{\bar{M}^2\bar{r}}{\bar{\rho}\bar{A}k} \tan {_c\alpha_2}}{\left(1 + \dfrac{\bar{M}r^2}{k}\right)} . \tag{10}$$

Note further that from the vector triangles and the assumed symmetrical conditions

$$\tan {_c\alpha_1} = 2{_c\phi} - \tan {_c\alpha_2}, \tag{11}$$
$$\tan {_t\alpha_1} = 2{_t\phi} - \tan {_t\alpha_2}. \tag{12}$$

Finally we define $\quad {_t\psi} = 2{_t\phi}(\tan {_t\alpha_2} - {_t\phi})$

and $\quad {_c\psi} = 2{_c\phi}(_c\phi - \tan {_c\alpha_2}). \quad (13)$

The stage total temperature rise is $_c\Delta T = \dfrac{_c\psi \cdot {_cv_a}^2}{_ck_p}, \quad (14)$

and the turbine temperature drop is $_t\Delta T = \dfrac{_t\psi \cdot {_tv_a}^2}{_tk_p}. \quad (15)$

Blade Performance

It remains now to consider, in more detail, the aerodynamic performance of the blades. For this we rely on cascade tests (2) in which a pack of blades is mounted in a wind tunnel and the angle α_2, and the losses of pressure are measured for a range of values of α_1 and M_{n1}. Such tests are two dimensional and when the results are applied to predict the flow in an annulus some care is necessary. It is found by experience (3), that the values of the leaving gas angle measured in two dimensional tests may safely be applied to the annular flow, whilst to the two dimensional loss measured must be added due allowance for annulus and wall friction loss, and also an allowance for the fact that the

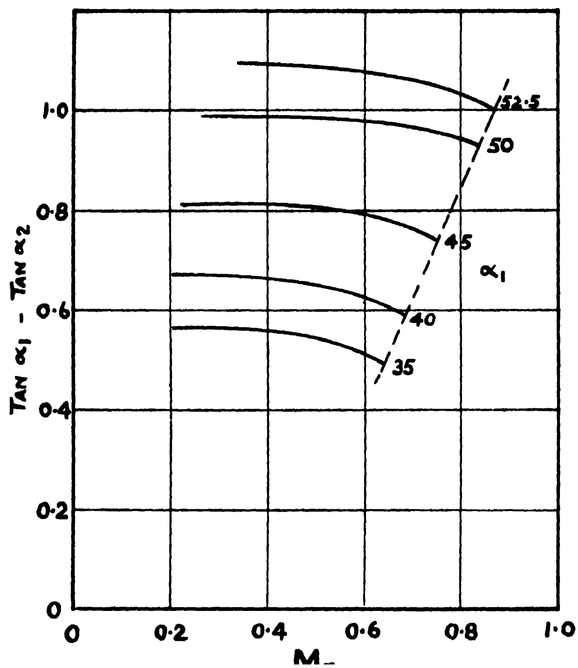

FIG. 3. *Compressor blade performance curves—section Gottingen 436, 50 deg. Camber,—20.5 deg. stagger.*

flow is in fact three dimensional and that there are slight variations in incidence up and down the blade, leading to secondary losses. These may be allowed for and in Fig. 3 we show a typical set of curves, relating the tangent of α_2 to tan α_1, and the Mach number. Fig. 4 shows the stage efficiency as a function of α_1 and Mach number.

A third factor to be considered is the value of the axial velocity. This may be calculated from the mass flow and area and density to give a mean value, but in practice the growth of the boundary layer in an adverse pressure gradient

increases the axial velocity above this value. This may be allowed for if necessary by putting in an empirical factor multiplying the right hand side of Equations (14) and (15), known as a work factor, or it may be taken care of by putting in a factor multiplying the nominal flow areas by a so-called contraction factor. Either, since the factors must be determined from analysis of test results, will yield reasonable results afterwards. The contraction factor is probably sounder physically.

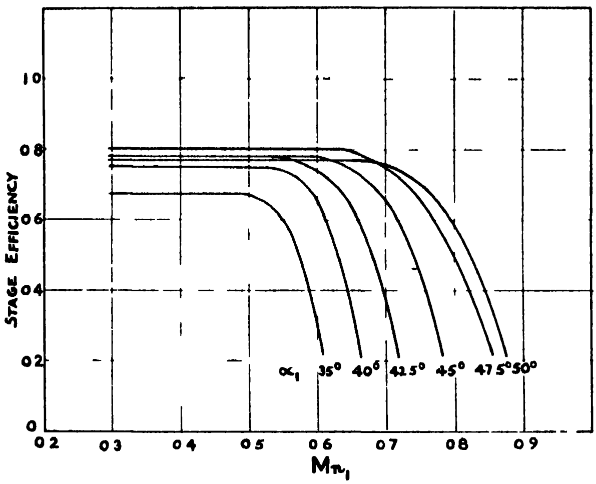

FIG 4. *Estimated compressor stage efficiencies, assuming annulus and secondary losses to be 150% of the minimum profile drag*

Performance Integration

We are now in a position to combine Equations (9) to (15) with the data of Figs. 3 and 4 and the corresponding data for the turbine blades to produce a complete performance analysis.

The combination of Equation (11), with Fig. 3, yields a relation between ${}_c\phi$, tan ${}_c\alpha_2$ and ${}_cMn_1$ which is shown on Fig. 5. There is a corresponding relation between ${}_t\phi$, tan ${}_t\alpha_2$, and ${}_tMn_1$, but in this case we do not show on Fig. 6 any variation due to ${}_tMn_1$, as in turbines of this kind, the turbine Mach numbers are always a long way from the critical values. From Figs. 5 and 6 we can solve Equation (9). For typical values of A and $\bar{r}$, and $\bar{M} = 1.0$ this is plotted on Fig. 7 as a curve of ${}_c\phi$ against ρ.

This is the key to the solution and there is no need to proceed in any detail further.

For any contraflow compressor of specified geometry we can prepare curves such as Figs. 7 and 8 for each rotor. Then our four independent variables are

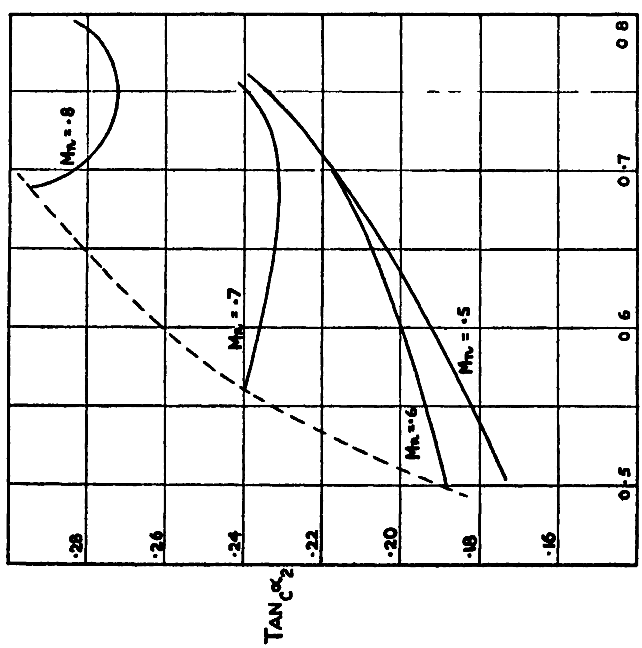

FIG. 5. *Compressor leaving angles as a function of* $_c\phi$ *and* $_cMn_1$.

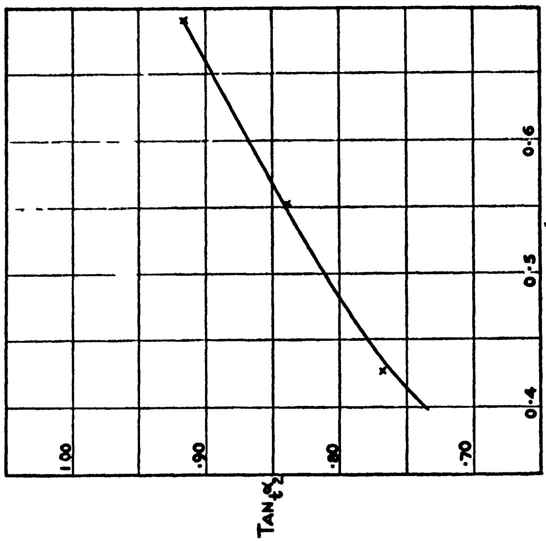

FIG. 6. *Turbine leaving angles as a function of* $_t\phi$.

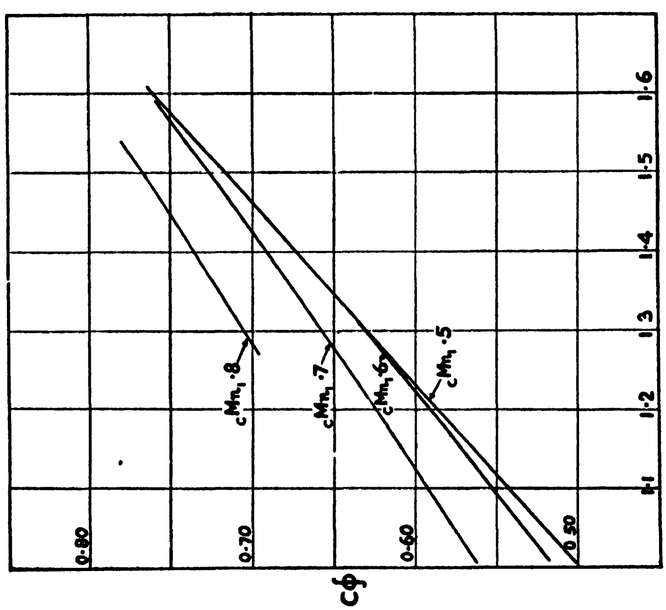

FIG. 7. *Relation between* $_c\phi$, $\bar{\rho}$ *and* $_cMn_1$ *at equilibrium running conditions*

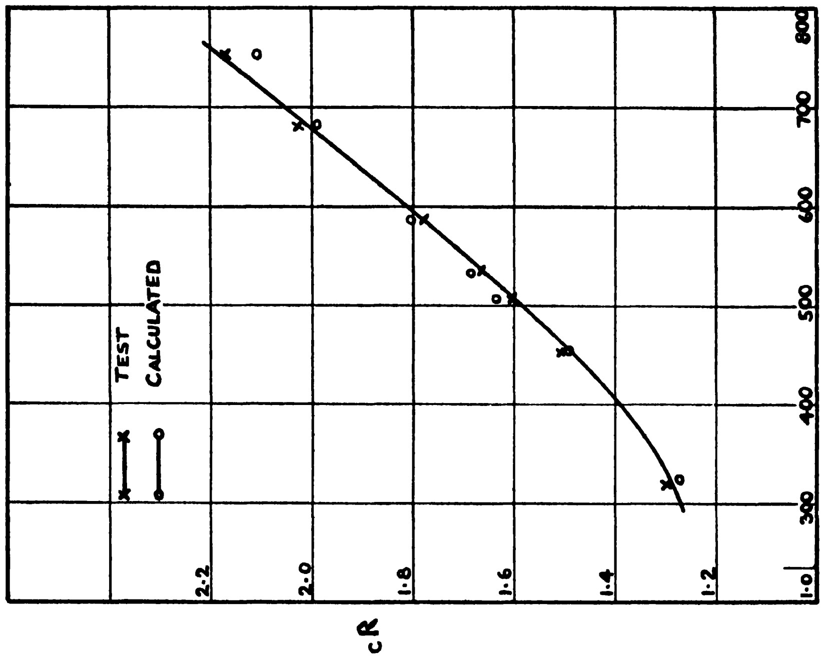

FIG. 8. *Comparison of predicted and measured variation of compression ratio with flame temperature.*

$_cM$, $_cp$, $\bar{p}$, and $\bar{M}$. The $\bar{p}$ is most conveniently expressed at the low pressure end of the unit. Then since $\bar{p}$ fixes $_c\phi$ and $_cM$ and $_cp$ fix $_cv_a$, all the conditions at the L.P. rotor are known, in particular all gas velocities and directions.

The value of $_c\psi$ gives us the temperature rise in the compressor stage, and Fig. 4 yields the stage efficiency, permitting the pressure ratio to be calculated. In a similar manner we can work backwards through the turbine stages. Thus we can calculate all the conditions on the far side of the L.P. rotor, which are then the entry conditions to the next stage, through which we can work in turn, and so on, integrating through all the compressor and turbine stages until the H.P. end is reached.

Example

To show the results obtained by the method, Figs. 8 and 9 compare the measured and calculated performance, for an experimental turbocompressor

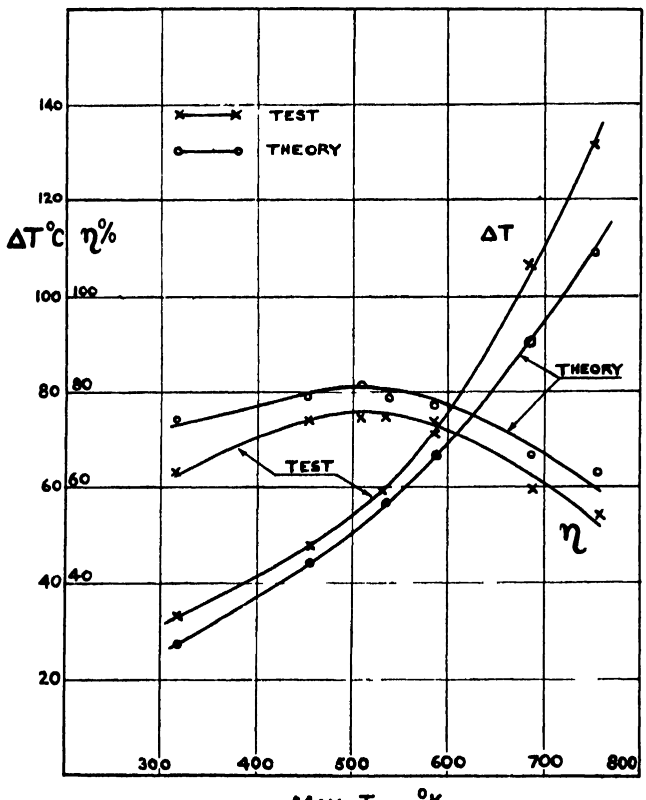

FIG 9. *Comparison of predicted and measured variation of compression temperature rise and efficiency with flame temperature.*

that was run at a constant value of $_cM$, $_cp$, and $\bar{M} = 1.0$, while $\bar{p}$ was varied. $\bar{p}$ was varied by varying the turbine entry temperature, and the results are plotted against this variable. It is evident that the compression ratio is in

close agreement. The observed temperature rise was greater than that predicted, which is the reason why the efficiency is low. The explanation of this can be seen by reference to the illustration of Fig 1. Any leakage between stages from turbine to compressor will raise the apparent temperature rise. Considering this effect, the agreement is regarded as satisfactory. Fig. 10

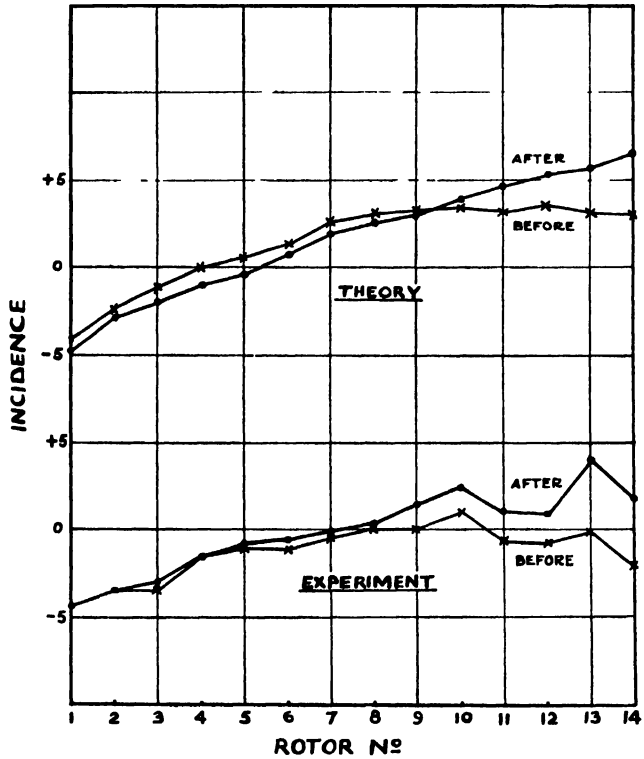

FIG 10 *Comparison of predicted and measured value of compressor blade incidence*

shows the calculated and observed values of the incidence on the compressor blades for all the rotors In this figure two sets of predicted and observed results are shown, as predictions were made of the estimated results following a modification in the turbine blades to alter their angles. Again the agreement is fairly satisfactory. It is interesting to note the peculiarities of the observed results at rotors Nos. 10 to 14. It will be remembered that the theory used neglects any effect of stator angle. In other words it assumes that the stator angle can be always adjusted to suit operating conditions. In fact, of course, a compromise is necessary, and the lower curves show the effect of the error introduced.

Application to Other Types of Unit

The method described applies particularly to a certain type of turbocompressor unit. With suitable modifications it is applicable to any type of compound engine, having one or more compressor stages each of which is

independently driven by its own turbine stage. In such cases, it often happens, if there are relatively few stages, that the turbine stages may be operating under "choked" conditions which makes calculation easier, by controlling the mass flow ${}_tM$.

Acknowledgments

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NOTES

Removal of Traces of Oxygen from Gases

For anaerobic studies in the Warburg apparatus, and for other purposes, it is often necessary to remove oxygen from commercial nitrogen or nitrogen—carbon dioxide gas mixtures. The method most commonly used consists in passing the gas over heated copper fragments in a combustion tube. The apparatus shown in the accompanying diagram and described below, has been found very convenient for this purpose. It is easily constructed, clean, relatively cool, easy to use, and occupies little laboratory space. Such apparatus has been used for several years in three laboratories.

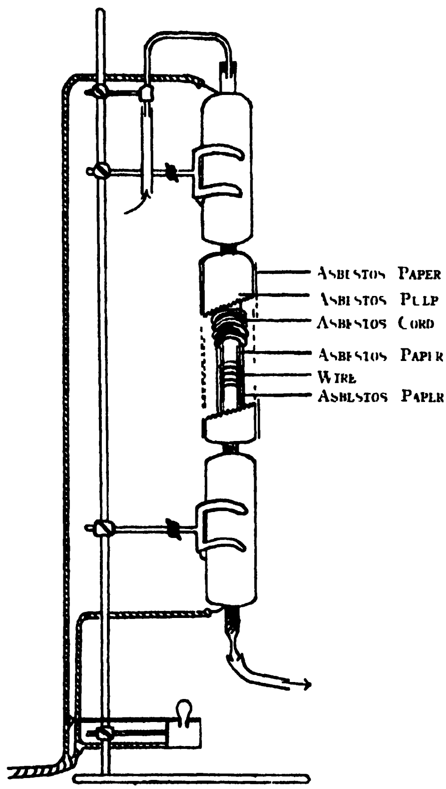

Fig. 1.

A tube of Pyrex No. 172 glass about 70 cm. long, 16 mm. inside, 20 mm. outside diameter, is drawn down at one end to a tip suitable for connection to rubber tubing. The tube is well packed with copper oxide wire fragments, which are held in place by rolls of copper gauze. The greater part of the length of the tube is wrapped with two layers of thin asbestos paper and then wound

evenly, 3 to 3.5 turns per cm., with nearly 40 ft. of Nichrome wire, 2 ohms per ft. Two more layers of asbestos paper are wrapped on, and over this a layer of asbestos cord is wound closely. An asbestos paste is prepared by crumbling ordinary steam pipe lagging with water. This paste is smeared and moulded onto the tube over the asbestos cord to a thickness of about 15 mm. After this has dried it is protected by a further layer of asbestos paper tied on with wire.

It is useful to make one or two windows in the windings so that the condition of the copper in the tube may be seen. To make these, one or two turns of the Nichrome wire and asbestos cord are spaced widely, and the layers of asbestos paper are cut away with a razor blade, except under the wire, before applying the asbestos paste to the remainder of the tube. The apparatus as described is used with 110 v. d-c. power source but 110 v. a.c. should be equally satisfactory. No external resistance is used except initially when it is advisable to put a lamp in series until the asbestos lagging has thoroughly dried. By means of a high temperature thermometer embedded in the copper fragments it was found that the temperature reached about 450°C. within 20 min. of turning on the current, and the maximum temperature was about 650° to 700°C.

To reduce the copper, hydrogen mixed with a carrier stream of nitrogen or other inert gas is passed through the hot tube. The tube takes an hour or more to cool after the power is disconnected and it is advisable to maintain a slight flow of inert gas through the tube until it is cool.

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K. A. C. ELLIOTT

DEPARTMENT OF NEUROLOGY AND NEUROSURGERY,
MCGILL UNIVERSITY, AND THE
MONTREAL NEUROLOGICAL INSTITUTE,
MONTREAL, QUE.

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THE IODINE CONTENT OF FRUITS AND VEGETABLES[1]

BY ROBERTA B. CAMPBELL[2] AND E. GORDON YOUNG

Abstract

The content of iodine in fruits and vegetables from the eastern Maritime Provinces has been determined by a modified Pfeiffer procedure. The sensitivity of the method was found to be about 1 μgm., with an accuracy of approximately ± 5%. The results obtained were near the mean values previously reported. The iodine content of potatoes varied from about 50 to 400 p.p b. with a mean value of 153 p.p b.; that of turnips from 50 to 90, several samples of cabbage, peas and pumpkin showed no trace of iodine present. Most specimens of fruit had no iodine, or only a trace, with the exception of plums which contained 113 p.p.b. No correlation of iodine content with variety or site of origin was evident.

Although numerous analyses of foods have been made for their content of iodine, very few have been carried out on foods of Canadian origin. This paper records analyses of iodine in the commoner fruits and vegetables from various districts of Nova Scotia and Prince Edward Island. These include several varieties of potatoes, turnips, carrots, parsnips, beets, squash, pumpkin, cabbage, cauliflower, corn, peas, beans, cucumber and tomatoes; apples, plums and pears.

Experimental

Material

Seventy-eight samples of apples and pears from the Annapolis Valley, N.S., 16 samples of potatoes from various parts of Nova Scotia and Prince Edward Island, 25 samples of various fruits and vegetables from different districts of Prince Edward Island, and 19 samples of still other fruits and vegetables from Nova Scotia, have been collected. Not all were analyzed, because of the insignificant amounts of iodine found to be present.

These samples were washed, sliced, and then dried for a period of 24 hr. at 40° C. They were stored in glass jars. Prior to analysis they were dried at 100° C. to constant weight and ground in a Wiley mill to pass a screen of No. 20 mesh. All samples of potatoes were prepared with skin. Turnips, squash, and pumpkin were peeled but other vegetables were analyzed as a whole. Plums were stoned but apples and pears were sliced and dried in their entirety.

[1] *Manuscript received in original from December 8, 1948, and, as revised, May 23, 1949. Contribution from The Department of Biochemistry, Dalhousie University, Halifax, N.S.*

[2] *Research Assistant.*

Method of Analysis

Many methods, differing in sensitivity depending on the amount of iodine present, have been developed for the estimation of iodine in biological material. Such methods require preliminary oxidation of organic matter, and no procedure has been generally accepted for this operation. Both dry and wet combustions have been used. Fusion with potassium hydroxide is very difficult with powders high in carbohydrate because of frothing and carbonization.

An attempt was made initially to follow the method of Kahane and Tomesco (3), who made use of a mixture of perchloric, nitric, and sulphuric acids for the digestion. The oxidation was not readily controlled and a violent explosion of unknown cause necessitated a modification of the procedure (6).

Oxidation, omitting the perchloric acid, was next attempted with a mixture of 3 ml. of concentrated nitric acid and 47 ml. of concentrated sulphuric acid to 1 gm. of dried sample. While this method gave correct results with recrystallized iodoform (99.2% recovery of iodine), with desiccated potato it required prolonged, careful heating. An attempt was made to carry out the digestion in an open vessel, as used by Chaney (1), but agreement in duplicate determinations was not satisfactory.

Digestion with concentrated sulphuric acid and 30% hydrogen peroxide by the method of Pfeiffer (4) was then tried. This procedure proved satisfactory as the initial stage. The estimation was completed by the method of Trevorrow and Fashena (5) and that suggested by Harvey (2), with certain modifications as described below. Replicate analyses were obtained at levels of iodine content of 100 p.p.b. or higher, with a precision of $\pm 2\%$. This decreased to about $\pm 5\%$ at lower levels of concentration. Recovery of known amounts of potassium iodide added to samples of potato was achieved with an accuracy of about 5%.

Reagents

Water and *ethanol* (95%) were distilled after the addition of a small amount of potassium carbonate in an all-glass still.

Potassium carbonate was made into a paste with distilled water and extracted with redistilled ethanol (95%). The residue was dried and made into a saturated solution in redistilled water.

Other reagents were found to be free of iodine.
Sulphuric acid, 20% v/v, 50% and concentrated, analytical grade.
Hydrogen peroxide, 30% analytical grade.
Bromine water, analytical grade in redistilled water.
Sodium thiosulphate, 0.1 N diluted each day to 0.001 N.
Potassium iodide, solid, analytical grade free of iodate.
Starch, 1%.

Principle

Organic matter is oxidized in the presence of concentrated sulphuric acid and relatively large amounts of hydrogen peroxide. In this procedure any iodine present is liberated as such. This is driven off by a combination of air and steam, to be trapped as potassium iodide and hypoiodite. The latter substances are oxidized to iodate by hot aqueous bromine and titrated as iodine, in the presence of acid and excess of potassium iodide, with standard thiosulphate.

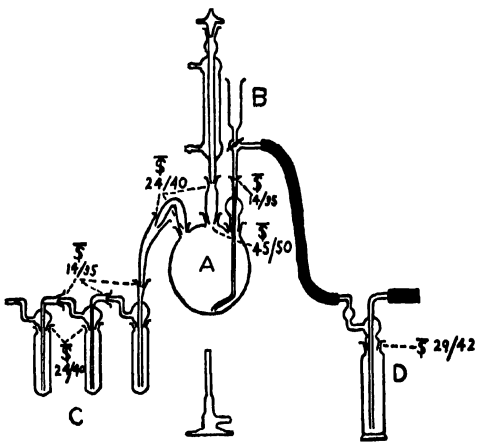

FIG 1. *Apparatus for oxidation of organic material and absorption of iodine liberated.*

Procedure

The apparatus was assembled for the most part of standard taper Pyrex glass parts as shown in Fig. 1. It consisted of a three-necked digestion flask (*A*) of 2 liters capacity. A reflux condenser, operated without water, was connected with the central neck and a glass stopper, standard taper 24/40, was inserted at the top of the condenser as shown. The gas-absorption tubes (*C*) were of 100 ml. capacity (obtained from the Scientific Glass Apparatus Co., Bloomfield, N.J., as parts of the distilling apparatus listed as J-1350). To each were added 10 ml. of a saturated solution of potassium carbonate and 40 ml. of redistilled water. A specially blown inlet tube (*B*) served for control of both liquid and air through a three-way stopcock. *D* is a gas-absorption bottle of 125 ml. capacity containing 50 ml. of aqueous sodium hydroxide (10%).

Twenty grams of dried sample was introduced into the digestion flask together with 200 ml. of 50% sulphuric acid. They were thoroughly mixed and the apparatus was connected as shown. Concentrated sulphuric acid (250 ml.) was added through inlet *B*. Compressed air was then slowly passed through the apparatus at a rate to ensure adequate mixing of the contents. Heat was applied at this point to the digestion flask, the amount of heat depending on the spontaniety of the reaction. Some samples did not require

any external application of heat until a large portion of the hydrogen peroxide had been added. This served to avoid excess foaming. Only a small flame from a Bunsen burner was used in the early stages of oxidation. Hydrogen peroxide (30%) was added slowly through *B* in small portions to an amount of about 75 ml., the actual amount being governed by the rate of the oxidation. When the rate of reaction was decreasing, heat was applied to the flask, and the remainder of the hydrogen peroxide, usually about 25 ml., was added slowly while the mixture was fuming. When the sample was oxidized completely, as indicated by loss of color in the digestion mixture, the absorption bulbs were disconnected. The contents were washed into an evaporating dish and taken to dryness on a water bath. The residue was extracted with ethanol and the extract evaporated to dryness. The residue was dissolved in water, 3 to 4 ml. of freshly prepared bromine water added, and the whole acidified with sulphuric acid (20%). This mixture was boiled until free from bromine and then cooled. It was titrated with 0.001 *N* sodium thiosulphate in a 1 ml. microburette, graduated in hundredths, after the addition of a few crystals of potassium iodide and 1 to 2 drops of starch (1%) as indicator. With the precautions outlined, a blank determination gave no color on the addition of the starch. The reaction is based on the equation

$$HIO_3 + 5HI \rightarrow 6I + 3H_2O$$

$$1 \text{ ml. } Na_2S_2O_3 \; 0.001\, N \approx 21.2\, \mu\text{gm. iodine } (1/6 \text{ of } 127).$$

The method has been found unsatisfactory by Trevorrow and Fashena (5) with fatty material. This difficulty has not entered into the present investigation because of the relatively insignificant amounts of lipid present.

Results

The analytical values obtained are recorded in Tables I and II. When the presence of iodine was detectable but so small as not to be measurable accurately, it has been recorded as a trace. On the basis of our technique this means less than 50 p.p.b. or 1 μgm. in 20 gm. of dried material. Results have been expressed in parts per billion on the basis of dry weight $\approx$ μgm. per kgm. The presence of 50 p.p.b. or less in a food is indicative of a relatively poor source of iodine from a nutritional point of view.

Table I records the analyses on 16 samples of potatoes in four known varieties. The average content of iodine was 153 p.p.b., assuming a trace to represent approximately 25 p.p.b. No single variety was consistently higher than others and no locality was notably better in this respect, with the possible exception of Prince Edward Island. The average figure for iodine in potatoes as given in the literature is about 177 p.p.b., but excluding one very exceptional value of 1,045 it becomes 134.

TABLE I

ANALYSES OF POTATOES

Source	Variety	Iodine content, p.p b.
Charlottetown, P.E.I.	Unknown	153
"	Irish Cobbler	363
"	"	369
Truro, N.S.	Unknown	< 50
Hall's Harbour, N.S	Irish Cobbler	< 50
"	Katahdin	114
Kentville, N.S.	Irish Cobbler	< 50
"	Green Mountain	401
"	Katahdin	143
"	Sebago	105
Scott's Bay, N.S.	Irish Cobbler	< 50
"	Green Mountain	66
"	Katahdin	114
"	"	109
"	Sebago	77
Halifax, N.S.	Unknown	334
		Average 153

TABLE II

ANALYSES OF VEGETABLES

Vegetable	Source	Variety	Iodine content, p p.b.
Beans	Charlottetown, P.E.I.	Unknown	< 50
	Alliston, P E.I.	Webber Wax	—
Beets	Alliston, P E I.	Detroit Dark Red	100
	Kensington, P.E I.	Unknown	—
	Charlottetown, P.E.I.	"	< 50
Cabbage	Truro, N S.	"	—
	Kentville, N.S.	"	—
	Charlottetown, P.E.I.	Golden Acre	—
Carrots	Alliston, P E I.	Hutchinson	50
	Charlottetown, P.E.I.	Chatenay	—
	Avonport, N.S.	Unknown	—
	Truro, N.S.	"	< 50
	Kentville, N.S.	"	< 50
Cauliflower	Charlottetown, P.E.I.	Snowball	—
Corn	"	Golden Bantam	< 50
Cucumber	"	Snowball	< 50
Parsnips	Kentville, N.S	Unknown	< 50
	"	"	—
Peas	Charlottetown, P.E.I.	"	—
	Kensington, P.E.I.	"	—
	Alliston, P.E.I.	"	—
Pumpkin	Charlottetown, P.E.I.	Small Sugar	—
Squash	"	Golden Hubbard	< 50
Turnips	Kentville, N.S.	Unknown	< 50
	Avonport, N.S.	"	91
	Truro, N.S.	"	50
	Charlottetown, P.E.I.	Laurentian	81

Table II records all analyses carried out on vegetables other than potatoes. Turnips showed a measurable amount of iodine and most samples exhibited a trace. No iodine was detected in cabbage, cauliflower, peas, or pumpkin. With the exception of potatoes and turnips, vegetables in the eastern Maritime provinces are not notable for their content of iodine. Other investigators have found appreciable amounts in cabbage, carrots, and squash in North America.

Eleven samples of apples from 10 localities in Nova Scotia have been analyzed. The varieties included Baldwin, Blenheim, Cox Orange, Golden Russet, Gravenstein, Kings, McIntosh Red, Red Stark, Ribson, Wagener, and Wealthy. Of these the Gravenstein and Red varieties contained a trace of iodine while the rest were negative. One variety of pears and one of tomatoes contained no iodine, but plums, as the Bradshaw variety, exhibited a value of 113 p.p m. These results are in conformity with those of other investigators, with the exception of the results for tomatoes, which have been found to vary markedly in their iodine content.

Discussion

It is apparent from the tables that fruits and vegetables from Nova Scotia and Prince Edward Island contain amounts of iodine comparable with median values as reported for other parts of the world. It is interesting to note that all samples that we have analyzed were harvested at a distance of less than 50 miles from the Atlantic ocean. This would suggest, a priori, a content of iodine above the general average, but this was not found to be true.

Acknowledgments

The authors wish to take this opportunity of expressing their thanks and indebtedness to Mr A. Kelsall, of the Dominion Experimental Station, Kentville, N.S., to Mr. J. A. Clark of the Dominion Experimental Station, Charlottetown, P.E.I., and to Mr. C. E. Bowlden of the Nova Scotia Agricultural College, Truro, N.S., for providing us with the various samples of fruits and vegetables used in this investigation.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

IX. THE CAUSE OF THE REVERSAL OF THE ANTIKNOCK PROPERTY OF RICH HYDROCARBON-AIR MIXTURES[1]

R. O. KING[2], W. A. WALLACE[3], AND E. J. DURAND[4]

Abstract

The experiments described show that conditions can be set in which a reversal of the antiknock effect of enriching a hydrocarbon-air mixture can be obtained in an unsupercharged engine. The reversal is of importance in respect of supercharged aero engines in which it may occur before mixture strength is increased to the value required for the development of maximum power. The experimental results, considered in the light of the nuclear theory of detonation, indicate that the "reversal" occurs when the rate of formation of finely divided carbon by pyrolysis of the fuel provides a proknock effect greater than can be offset by the antiknock effect of the products of the high temperature heterogeneous oxidation reaction.

Introduction

The increase in usable compression ratio obtained on increasing mixture strength is due, aside from the cooling effect, to the corresponding increase in rate of surface oxidation of the fuel to antiknock products, Part VIII (3). Dilution of the end gas by the products lowers inflammability and offsets the tendency to nuclear ignition arising from impregnation of the end gas by finely divided carbon derived from pyrolysis of the hydrocarbon fuel, Part IV (2).

The increase of end gas temperature as compression ratio is raised and an increase in the concentration of hydrocarbon fuel in the mixture with air lead to an increase in rate of pyrolysis. It would be expected, therefore, that when using fuels prone to pyrolysis in high temperature conditions of engine operation the increased tendency to nuclear ignition might cease to be offset by the decrease in inflammability of the end gas arising from dilution with the products of high temperature surface oxidation. A *reversal* of the antiknock property of rich mixtures would then occur.

The object of the experiments described in this Part was to obtain the "reversal" in the conditions in which it would be expected to occur according to the theories mentioned.

[1] *Manuscript received March 5, 1949.*
Contribution by Defence Research Board (Canada) and the Department of Mechanical Engineering, University of Toronto, Toronto, Ont.

[2] *Research Scientist, Naval Division, Defence Research Board, and Honorary Lecturer, Department of Mechanical Engineering, University of Toronto; lately Director of Scientific Research and Development, Royal Canadian Navy.*

[3] *Assistant Professor of Mechanical Engineering, University of Toronto.*

[4] *Lecturer in Mechanical Engineering, University of Toronto.*

Experimental Arrangements and Selection of Hydrocarbon Fuel

The C.F.R. knock testing engine, unsupercharged, was used for the experiments in the manner described fully in Part VIII (3). The sole change was the provision of larger diameter fuel flow control orifices as required for increasing mixture strength beyond the degree used for the standard method of knock rating.

The high temperature operating conditions expected to be required were provided by the standard A.S.T.M. - C.F.R. motor method of knock rating, that is, the fuel-air mixture was heated to 300° F. and the jacket coolant maintained at 212° F.

Preliminary experiment demonstrated that a reversal of the antiknock property of rich mixtures of normal heptane, hexane, or pentane with air could not be obtained even in the relatively high temperature operating conditions. An indication of the effect was obtained, however, when the compression ratio at which heptane could be used was increased, on the addition of tetraethyl lead.

Fuel *S* was then used for further experiments. It is a commercial gasoline of relatively high octane number as compared with *n*-pentane. The distillation graph, given by Fig. 1, Part VIII (3), shows an end point of 429° F. and that the fuel contains approximately 30% of constituents boiling above 300° F. The "heavy ends", probably long chain paraffins, would be especially prone to yield carbon on decomposition at the high temperatures of the end gas.

One set of experiments was made with fuel S_1, generally similar to fuel *S* but of lower initial octane number raised to exceed that of fuel *S* by being leaded. Unleaded fuel S_1 could not be obtained.

Experimental Results

The experimental results are given by the graphs of Fig. 1, compression ratio for standard knock intensity, described as "usable compression ratio", being plotted against rate of fuel consumption, which represents mixture strength, engine speed being constant at 900 r.p.m. The minimum value of usable compression ratio for the undoped fuel *S* was obtained when rate of fuel consumption was 1.85 lb. per hr. and it may be assumed that the mixture strength was then approximately correct. Maximum power, determined by later experiments, was obtained when rate of fuel consumption was 2.4 lb. per hr. The mixture was then nearly 30% "rich".

The reversal of the antiknock property of rich mixtures of fuel *S* undoped, Graph (1), was obtained when the usable compression ratio attained the high value of 8.2, rate of fuel consumption being then 3.7 lb. per hr. and the mixture 100% rich. On adding tetraethyl lead to fuel *S* in the concentration of 0.25 cc. per liter the "reversal" occurred at the higher usable compression ratio

of 9.3 but at the lower rate of fuel consumption of 3.4 lb. per hr., the mixture then being 84% rich. A similar "reversal" was obtained at a relatively low rate of fuel consumption when using fuel S_1, Graph (2). Comparable results for this fuel undoped are not given because a sample was unobtainable, as already mentioned.

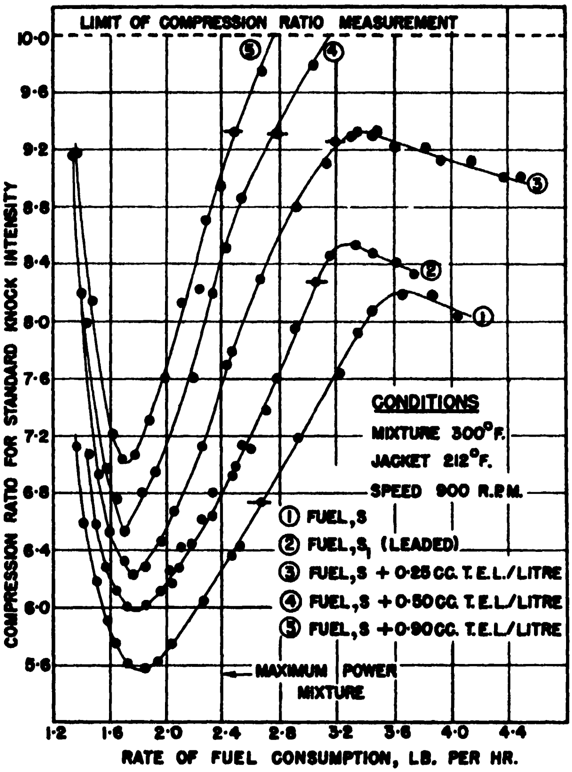

FIG. 1. *Graphs showing the reversal of the antiknock effect of rich mixtures.*

When tetraethyl lead was added to fuel S in the larger concentrations of 0.5 and 0.9 cc. per liter, usable compression ratio, Graphs 4 and 5, exceeded the 10:1 measurement limit before a "reversal" occurred.

The short horizontal lines on the graphs indicate the beginning of preignition which, however, never became sufficiently continuous to enable the engine to run with the spark ignition switched off.

Reversals of the antiknock property of rich mixtures were obtained when fuel S contained iron or nickel carbonyl. The experimental results were so nearly like those, shown graphically by Fig. 1, for fuel S leaded that they need not be described.

Discussion

The rate of formation of antiknock products by high temperature heterogeneous oxidation reactions in an engine is limited by the available area of active surface. On the other hand the rate of formation of proknock finely divided carbon by pyrolysis of the hydrocarbon fuel increases with the *quantity* inducted per stroke. The experiments described show that on increasing the quantity by using sufficiently rich mixtures a reversal of the antiknock effect of such mixtures was obtained in an unsupercharged engine, for the first time on record so far as known.

The reversal would be expected, according to the theory advanced, to occur in high duty supercharged engines when using leaner mixtures because the quantity of fuel inducted per stroke depends on supercharge pressure as well as on mixture strength. Thus if the combustible mixture be supplied at a pressure of say two atmospheres, the tendency to the formation of proknock carbon is doubled, other things being equal, while the rate of the heterogeneous reaction producing antiknock compounds remains unchanged. The consequence is that in supercharged aero engines, which are commonly operated in high temperature conditions, a reversal of the antiknock effect of enriching the mixture may occur even before the attainment of the mixture strength required for maximum power.

The factors leading to the reversal seem to have first received attention in Germany, and developments have accordingly been described recently by Petty, Wright, and Garner (5, 6). Recent N.A.C.A. experimental work dealing with the subject has been described by Genco and Drell (1) and by Lord, Heinicke, and Stricker (4). The cause of the reversal effect is not discussed in the references mentioned.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and the cost defrayed in part by an extramural grant from the Defence Research Board (Canada). The liberality of Ethyl Corporation in respect of the supply of Ethyl fluid and pure tetraethyl lead is gratefully acknowledged.

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CANADIAN ERUCIC ACID OILS

IV. EDIBLE PROPERTIES OF FANWEED (PENNYCRESS) OIL AND SHORTENING[1]

BY H. J. LIPS[2] AND N. H. GRACE[2]

Abstract

Salad oils and shortenings prepared from crude fanweed seed oil by standard methods were lighter in color and more viscous than corresponding commercial products tested, and had slightly lower smoke points. Peroxide oxygen values and free fatty acid contents of all the materials were similar. Small-scale consumer acceptance tests indicated that the fanweed oils, either fresh or aged for 10 days at 100°F., were generally not as palatable as the commercial salad oils (corn and cottonseed), but that the fanweed shortenings did not differ appreciably from the commercial vegetable shortenings. It is concluded that the small amount of fanweed oil present in mixed oil from weed seed screenings will not lessen the potential acceptability of the mixture.

Introduction

The possibility of using Canadian grown rape and mustard seed oils as edible fat sources was suggested in earlier publications (2, 3, 5, 6).

Thlaspi arvense (fanweed, pennycress, French weed, or stinkweed), a member of the Cruciferae (to which rape and members of the mustard family also belong), grows abundantly on the Canadian prairies, and 13% of the weed seed screenings removed from grain crops consists of fanweed seed (4). The oil from such screenings is presently being extracted at Fort William, and uses are being sought for it.

Fanweed seeds contain 33 to 35% oil by weight. The oil is said to be similar in properties to rapeseed oil, and in Russia some consideration has been given to its use as an edible product (1). Consumer reaction to salad oil and shortening prepared from fanweed oil by standard methods therefore appeared to warrant attention.

Materials and Methods

The fanweed seed (300 lb.) used in this investigation was supplied by the Field Crops Commissioner of the Province of Saskatchewan. It was accum-

[1] *Manuscript received May 2, 1949.*
Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa, Canada. Issued as Paper No. 233 of the Canadian Committee on Food Preservation, and as N.R.C. No. 1978.

[2] *Biochemist, Oils and Fats Laboratory.*

ulated from screenings, and contained a small amount of broken flax, and other seeds such as rape, mustard, and lamb's-quarters (total impurities were less than 5%).

The seed was ground in a Hobart mill and the oil extracted in a large all-glass Soxhlet apparatus with petroleum ether (b.p. 85° to 140°F.). Part of the solvent was boiled off, and the rest removed under reduced pressure. The oil obtained was alkali refined, bleached, and deodorized to produce a salad oil; or refined, bleached, hydrogenated to shortening consistency, and then deodorized, as previously described (5, 6). Each test product was a composite of two or three independent preparations. Commercial salad oils (corn and cottonseed) and vegetable shortenings of good quality were used as reference materials in all tests, and comparisons were made both with fresh oils and shortenings and with oils and shortenings aged for 10 days at 100°F.

Color, fluorescence, kinematic viscosity, peroxide oxygen, free fatty acid, smoke point, melting point, and iodine value were determined for these materials (5, 6). Oils and shortenings were used in the preparation of mayonnaise, pastry, and doughnuts, as in earlier tests (5, 6), except that the amount of oil in the mayonnaise was reduced from about 80% to about 65%. Palatability attributes were scored by a panel of 24 individuals recruited from technical and administrative personnel, on a scale of 11 gradations of appraisal (−5 through zero to +5) ranging from "gross deficiency" through "preferred" to "gross excess".

Results

Characteristics of Oils and Shortenings

The experimental and commercial materials tested were generally similar in melting point and iodine value (Table I). Table II shows chemical and physical characteristics of representative products at various stages of use. The relative light transmissions of the fresh fanweed products were higher than

TABLE I

MELTING POINT AND IODINE VALUE OF TEST SAMPLES

Material	Melting point, °C.	Iodine value
Corn oil	.	122 7
Cottonseed oil	.	114.1
Fanweed oil	. .	120.6
Commercial shortening No. 1	38 0	57.4
Commercial shortening No. 2	42 8	66.7
Fanweed shortening No. 1	44 0	64.8
Fanweed shortening No. 2	42.7	71.0

TABLE II

CHEMICAL AND PHYSICAL CHARACTERISTICS OF OILS AND SHORTENINGS AT VARIOUS STAGES OF USE

Characteristic	Test material	Condition of test material			
		Fresh*	Aged	Fresh, fried	Aged, fried
Light transmission, per cent at 440 mμ relative to mineral oil (Stanolax)	Corn oil	29	27	26	27
	Cottonseed oil	54	55		49
	Fanweed oil	65	66	48	46
	Commercial shortening	67	66	50	56
	Fanweed shortening	74	73	37	38
Fluorescence, Coleman photofluorometer units, 1 gm of oil in 100 ml xylol, corrected for fluorescence of xylol	Corn oil	51	53	47	48
	Cottonseed oil	18	18		22
	Fanweed oil	17	17	21	19
	Commercial shortening	18	18	22	22
	Fanweed shortening	14	14	27	27
Viscosity, centistokes at 130°F	Corn oil	17 0	17 3	17 4	17 7
	Cottonseed oil	17 9	17 9		18 8
	Fanweed oil	20 7	20 3	21 1	21 0
	Commercial shortening	23 5	23 7	23 6	23 8
	Fanweed shortening	26 6	26 6	26 8	26 9
Peroxide oxygen value, ml of 0 002 N thiosulphate per gm	Corn oil	1 7	1 9	3 2	4 3
	Cottonseed oil	5 6	13 7		6 3
	Fanweed oil	0 0	5 4	1 8	6 4
	Commercial shortening	0 0	0 0	2 8	4 9
	Fanweed shortening	0 0	0 0	3 2	5 3
Smoke point, °F	Corn oil	410	406	408	398
	Cottonseed oil	442	446		440
	Fanweed oil	396	383	390	386
	Commercial shortening	419	417	413	405
	Fanweed shortening	388	390	375	390

**The commercial salad oils (corn and cottonseed) and the commercial shortenings were used as purchased and received no further processing*

those of the commercial ones at 440 mμ; but all values were about 97% at 660 mμ, so these are not presented. Light transmission of all products at 440mμ was not changed by aging, but decreased with use for deep fat frying of doughnuts. Fluorescence in ultraviolet light (375 mμ) generally increased with frying, except for corn oil, which showed a decrease. The fanweed oil and shortening were more viscous than the corresponding commercial products, and viscosities remained practically constant throughout the experiment. Peroxide oxygen content was zero in the shortenings, increased in the oils on aging, and increased in both the oils and shortenings on frying. Free fatty acid contents,

as per cent oleic, did not exceed 0.2%, so are not shown. The fanweed oil and shortening had lower smoke points than the commercial products and smoke points were generally decreased slightly by both aging and frying. In all these measurements the fanweed oil and shortening did not exhibit any important differences from the corresponding commercial products.

Subjective Appraisals

In two different appraisals of fresh samples, fanweed oil was considered too light in color, and corn oil too dark (Table III). Fanweed oil was rated as

TABLE III

AVERAGE SCORES RECORDED IN SUBJECTIVE APPRAISALS OF FRESH VEGETABLE OILS

Attribute	Average score		Necessary difference (5% level of statistical significance)	
	Corn oil	Fanweed oil	Between any two av.	Of any one av. from zero
Experiment 1				
Color	+0.6	−1.6	0.8	0.6
Texture	+0.1	0.0	0.6	0.4
Odor	0.0	0.0	0.5	0.4
Flavor	+0.7	+0.3	1.0	0.7
Experiment 2				
Color	+1.1	−1.3	0.5	0.4
Texture	0.0	−0.5	0.4	0.5
Odor	+1.3	−0.1	0.6	0.5
Flavor	+1.5	+1.0	0.7	0.6

slightly lacking in texture in one experiment, although its viscosity was higher than that of corn oil. Corn oil odor was considered too strong in one appraisal. Both fanweed and corn oils were assessed as having a slight excess flavor, but did not differ significantly in this respect. Pastry and doughnuts prepared with fresh oils and shortenings were given generally satisfactory odor scores in two separate experiments (Table IV). Flavor scores were mostly good when the commercial products or fresh fanweed shortening were used, but were relatively poor with fresh fanweed oil.

Aged, independently processed fanweed oils were rated approximately equal in color, texture, and odor to each other and to aged cottonseed oil, but differed in flavor from each other and from the two aged commercial oils (Table V). The attributes of the corn oil were all appraised as "excessive" in varying degrees.

TABLE IV

AVERAGE SCORES RECORDED IN SUBJECTIVE APPRAISALS OF PASTRY AND DOUGHNUTS MADE WITH FRESH VEGETABLE OILS AND SHORTENINGS

Attribute	Average score				Necessary difference (5% level of statistical significance)	
	Corn oil	Fanweed oil	Commercial shortening	Fanweed shortening	Between any two av.	Of any one av. from zero
Experiment 1						
Pastry odor	+0.3	+0.4	+0.5	+0.2	0.4	0.3
Pastry flavor	+0.4	+1.0	+0.4	+0.3	0.5	0.4
Doughnut odor	0.0	+0.3	+0.1	0.0	0.2	0 2
Doughnut flavor	0.0	+0.6	+0.1	+0.1	0.3	0.2
Experiment 2						
Pastry odor	+0.1	+0.4	−0.2	−0.6	0.4	0 3
Pastry flavor	+0.5	+2.0	−0.1	−0.8	0.6	0.5
Doughnut odor	+0.3	+0.2	−0.2	+0.4	0.4	0.4
Doughnut flavor	+1.0	+1.2	−0.3	+0.7	0.6	0.6

TABLE V

AVERAGE SCORES RECORDED IN SUBJECTIVE APPRAISALS OF AGED VEGETABLE OILS

Attribute	Average score				Necessary difference (5% level of statistical significance)	
	Corn	Cottonseed	Fanweed No. 1	Fanweed No. 2	Between any two av.	Of any one av. from zero
Color	+0.9	−0.2	−0.6	−0.4	0 3	0.3
Texture	+0.3	−0.1	−0.4	−0.1	0.3	0.3
Odor	+1.1	−0.3	−0.3	−0.4	0.4	0.4
Flavor	+1.6	−0.1	0.0	+0.7	0.5	0 5

Mayonnaises incorporating the aged fanweed and cottonseed oils were scored as similar in color, texture, and odor (Table VI). Corn oil mayonnaise was rated as slightly in excess in all the attributes under examination. Mayonnaise made with aged fanweed oil had the least satisfactory flavor.

Pastry and doughnuts made with aged fanweed oils were less palatable than those made with the aged commercial oils (Table VII), although excess odor

TABLE VI

AVERAGE SCORES RECORDED IN SUBJECTIVE APPRAISALS OF MAYONNAISE INCORPORATING AGED VEGETABLE OILS

Attribute	Average score				Necessary difference (5% level of statistical significance)	
	Corn	Cottonseed	Fanweed No 1	Fanweed No 2	Between any two av	Of any one av from zero
Color	+0 5	+0 1	+0 1	0 0	0 2	0 3
Texture	+0 5	0 0	−0 1	−0 2	0 3	0 4
Odor	+0 6	−0 2	0 0	0 0	0 4	0 4
Flavor	+0 6	0 0	+0 8	+1 0	0 5	0 5

TABLE VII

AVERAGE SCORES RECORDED IN SUBJECTIVE APPRAISALS OF PASTRY AND DOUGHNUTS MADE WITH AGED VEGETABLE OILS

Attribute	Average score				Necessary difference (5% level of statistical significance)	
	Corn	Cottonseed	Fanweed No 1	Fanweed No 2	Between any two av	Of any one av from zero
Pastry odor	+0 2	0 0	+0 4	+0 7	0 4	0 4
Pastry flavor	0 0	−0 4	+1 5	+1 7	1 0	0 6
Doughnut odor	+0 3	+0 3	+0 7	+0 5	0 5	0 5
Doughnut flavor	+0 3	0 0	+1 6	+1 0	0 5	0 5

TABLE VIII

AVERAGE SCORES RECORDED IN SUBJECTIVE APPRAISALS OF PASTRY AND DOUGHNUTS MADE WITH AGED VEGETABLE SHORTENINGS

Attribute	Average score				Necessary difference (5% level of statistical significance)	
	Commercial No 1	Commercial No 2	Fanweed No 1	Fanweed No 2	Between any two av	Of any one av from zero
Pastry odor	+0 1	−0 2	−0 1	+0 2	0 4	0 3
Pastry flavor	−0 3	−0 1	−0 4	−0 2	0 4	0 4
Doughnut odor	0 0	0 0	0 0	+0 2	0 3	0 3
Doughnut flavor	0 0	−0 1	0 0	+0 2	0 4	0 3

and flavor were found only in slight or moderate amounts. Aged fanweed shortenings, on the other hand, were as acceptable as the corresponding commercial shortenings (Table VIII).

Conclusions

Fanweed oil and shortening processed by standard methods did not differ appreciably from commercial salad oils and vegetable shortenings in most of the chemical and physical properties studied, and the few differences found are not regarded as important. Fanweed oil was generally not as palatable as corn or cottonseed oils, perhaps because of some tendency to flavor reversion, but appraisals of the palatability of fanweed shortening did not differ significantly from those of commercial hardened products. Hence, it is concluded that the small amount of fanweed oil present in mixed oil from weed seed screenings will not lessen the potential acceptability of the mixture.

Acknowledgments

The statistical aid of Dr. J. W. Hopkins, the technical supervision of odor and flavor appraisals by Miss E. M. Hamilton, and the technical assistance of Miss K. Stewart and Mr. A. C. Bell are all gratefully acknowledged.

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STOPCOCK LUBRICANTS[1]

By J. R. Farnand[2] and I. E. Puddington[2]

Abstract

The addition of appropriate quantities of finely divided solids to hydrocarbon, silicone, and glycerol base lubricants has been found to increase their life in stopcocks manyfold. The flow properties of the dispersions show that those solids that materially increase the high shear viscosity, without contributing greatly to the thixotropy of the system, are the most effective. This effect is produced by solids that have a polarity similar to that of liquid vehicle and are readily wetted by the vehicle. Under these conditions, a linear relation exists between the viscosity of the lubricants at a mean rate of shear of 1000 sec.$^{-1}$ and their life in the stopcock.

Introduction

A major shortcoming of available stopcock lubricants lies in their inability to provide permanent lubrication of the moving parts. Periodic lubrication, especially in low pressure systems, besides being a nuisance is frequently inconvenient and time consuming. While the development of a permanently lubricated, gas tight stopcock would be ideal, formulations that provide increased service life are worth while. The present investigation was initiated to determine what properties are necessary to ensure long service, and to examine means of increasing the life of currently available lubricants. Commercial preparations vary in consistency from very soft greases to heavy plastic solids, and their life in stopcocks is equally variable. Since it seemed probable that a relation existed between consistency and service life, both the flow properties and lubricating value were measured for a number of greases, with rather interesting results.

Experimental

The flow properties of the various lubricants were examined by weighing the amounts extruded in a given time from a steel capillary of 0.1648 cm. inside diameter and 2.545 cm. long. A range of pressures was supplied by compressed nitrogen and suitable reducing valves. The extruder was maintained automatically at a temperature of 30° ± 0.05°C. The apparent viscosity was calculated from Poiseuille's equation and the rate of shear was taken to be $\frac{4v}{\pi r^3 t}$, where the symbols have their usual meaning.

The lubricating values of the greases were determined as follows. The female part of a $\frac{29}{42}$ standard taper ground glass joint was clamped vertically in a block of wood. A length of wire with a 2 kgm. weight attached was passed through the axis and secured to the top of the male part. This provided a uniform

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[2] *Chemist.*

pressure on the moving member for subsequent experiments. A side arm sealed to the moving part served as a handle. After the joint was lubricated, the handle was turned through 90° and back to its original position. The number of such cycles that could be made before noticeable seizure of the joint or streaking of the lubricant occurred was noted, and the mean of several such determinations was recorded as the lubricating value of that lubricant.

Results and Discussion

Since nearly all the samples examined were thixotropic in some degree, the experimental results were treated to separate the viscous from the thixotropic effects. This was done by plotting the apparent viscosity against the reciprocal of the rate of shear and proceeding as suggested by Goodeve and Whitfield (2).

Typical results for the greases examined are shown in Fig. 1, where a considerable range, both in degrees of thixotropy and viscosity for any rate of shear, will be observed.

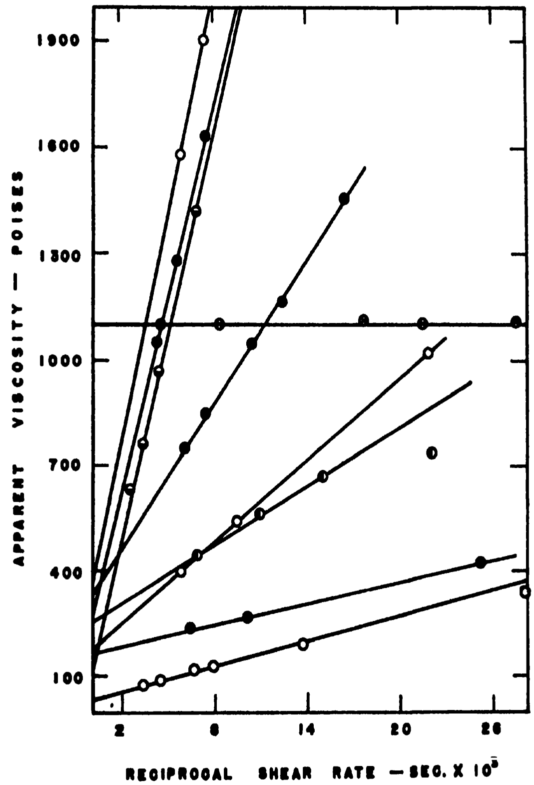

FIG. 1. *Typical data for various lubricants. Radial curves in a clockwise direction represent respectively, Dow-Corning lubricant plus 18% silica, hydrocarbon oil plus 25% lithium stearate, Cello-grease, Dow-Corning lubricant plus 10% silica, oil plus 15% lithium stearate, oil plus 25% carbon, Apiezon L, and Dow-Corning lubricant. Horizontal curve, glycerol plus 25% silica.*

It soon became apparent that the degree of thixotropy of a grease had little bearing on its life in a stopcock and that the lubricating value was due almost entirely to the high shear viscosity. The mean rate of shear in the joint under the conditions used in the experiment was estimated to be about 1000 sec.$^{-1}$ and the viscosities under this condition were compared with the lubricating value.

In spite of what has been said it is desirable that stopcock lubricants possess a fair degree of thixotropy, since otherwise the lubricant would flow continuously from the joint under the influence of gravity—or atmospheric pressure in the case of a vacuum stopcock. Further, this property is, in general, much less sensitive to temperature changes than is viscosity, and the thinning out that is noted in hot weather with some lubricants can be reduced considerably.

Although the early results indicated that the useful life of a grease in a stopcock was proportional to its high shear viscosity, a few samples were found that gave less service than that predicted. This was found to be due to gel formation, which tended to cause the material to flow through the capillary as a plug or agglomerates, and led to a false viscosity. Milling these samples for some time on an experimental rubber mill, or subjecting them to the high shearing action of a colloid mill prior to extrusion, put them in the predicted position.

Stopcock greases were, until recently, usually thickened hydrocarbons. Pure hydrocarbons having a natural high viscosity are quite satisfactory at room temperatures but, owing to their high temperature coefficient of viscosity, become scarcely usable when a temperature range of a few degrees has been exceeded. For maximum life and usefulness the thickening agent used should be finely divided and contribute only slight thixotropic properties, while adding a large bulk of inert solid to the vehicle. Kruyt and others (3) have shown that this effect is obtained when a solid highly wetted by the vehicle is used. For hydrocarbons an obvious choice is carbon or a very high melting hydrocarbon. Finely divided carbon is available in the form of Shawinigan black and the effect of its addition to a pure hydrocarbon oil having a viscosity of 3500 S.U.S. at 100°F. is shown in Table I. Since the particles adhere to one another tenaciously in the solid state, the carbon black must be added slowly to the oil and the mix well milled during the preparation. Its thixotropic contribution is not high and once a heavy paste has been broken down it recovers but little.

As solids of this sort are not affected by temperature, the viscosity–temperature properties of the liquids are much improved. The vapor pressure of such a preparation is, of course, governed by the liquid used.

Soaps have been used for a long time in the preparation of commercial lubricating greases. Of the soaps, lithium stearate is least affected by temperature changes and its use in conjunction with hydrocarbon oil has been suggested for stopcock lubrication (5). Results obtained with two concentra-

pressure on the moving member for subsequent experiments. A side arm sealed to the moving part served as a handle. After the joint was lubricated, the handle was turned through 90° and back to its original position. The number of such cycles that could be made before noticeable seizure of the joint or streaking of the lubricant occurred was noted, and the mean of several such determinations was recorded as the lubricating value of that lubricant.

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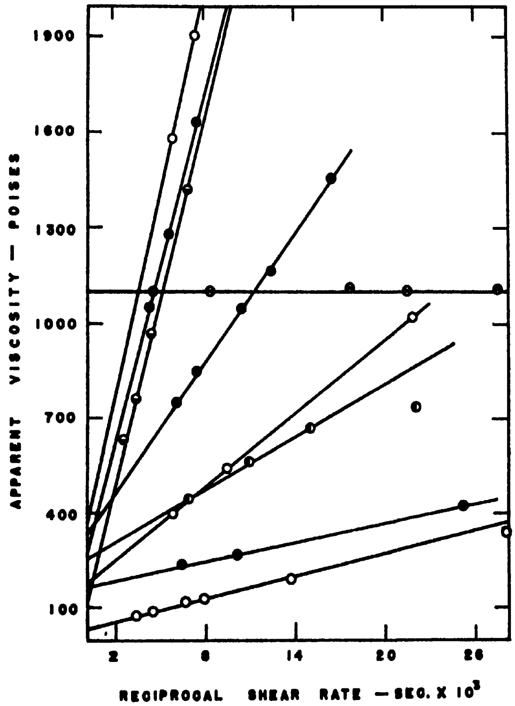

FIG. 1 *Typical data for various lubricants Radial curves in a clockwise direction represent respectively, Dow-Corning lubricant plus 18% silica, hydrocarbon oil plus 25% lithium stearate, Cello-grease, Dow-Corning lubricant plus 10% silica, oil plus 15% lithium stearate, oil plus 25% carbon, Apiezon L, and Dow-Corning lubricant. Horizontal curve, glycerol plus 25% silica*

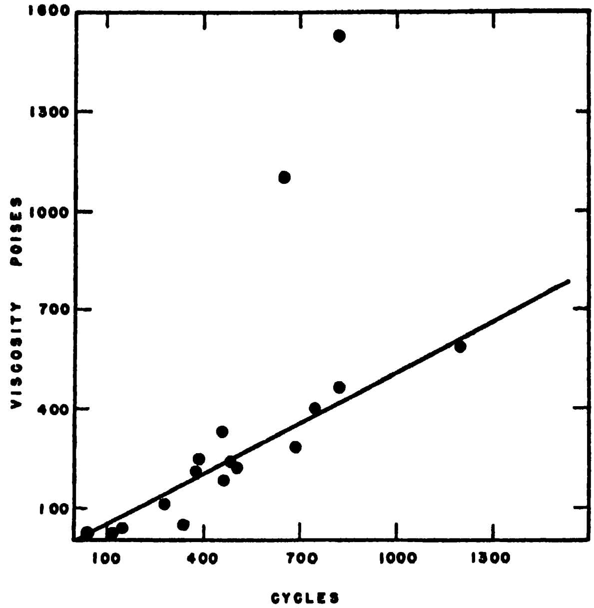

FIG. 2 *Variation in service life with high shear viscosity.*

The high concentrations of both pure and contaminated silica in glycerine had a service life far less than that predicted from viscosity data These were the only exceptions (Fig 2) and no explanation for the behavior can be offered at this time Two examples are also shown in Table I of quite highly thixotropic systems—carbon black in glycerine As expected these were inferior to silica

Low vapor pressure silicone compounds have recently become available as stopcock lubricants In view of their ability to wet silica an attempt was made to incorporate silica into them in various concentrations The striking effect on the viscosity and life as a lubricant is shown in the table

All of the experimental results are summarized in Table I and in Fig 2, which shows the general linearity in the relation between high shear viscosity and lubricating value The higher concentrations of solids used here may produce greases that are too viscous for all except very special uses When using those samples having extremely high viscosity, the stopcocks of necessity are turned slowly

The results of the work demonstrate feasible improvements that can be made in available lubricants both in temperature resistance and in useful life in the joints and give a possible basis for future developments

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THE SUSPENDING POWER AND VISCOSITY OF CARRAGEENIN[1]

By R. C. Rose[2] and W. H. Cook[3]

Abstract

This work indicates that the essential factor in suspending cocoa in milk is to increase the viscosity of milk to the point where cocoa does not settle, e.g., 15 centistokes at 10°C. in the system studied. For 21 samples of carrageenin the correlation coefficient between viscosity in milk and suspending power was .98. The high viscosity of cold milk containing as little as 0.04% carrageenin appears to be due to the formation of a casein–carrageenin gel, which is heat sensitive. With 0.1% carrageenin the gel separated into curd and whey when stirred. The correlation coefficient between suspending power in milk and viscosity in 0.05 *N* sodium chloride was .91; this suggests that the latter could be used to predict the former.

Introduction

Carrageenin, the dried, hot water extract of a red seaweed (*Chondrus crispus*) is used commercially as a suspending agent, particularly for suspending fine cocoa powder in chocolate milk. Little is known about the mechanism of this stabilization and estimates of suspending power are generally based on empirical tests of the minimum amount of carrageenin required to achieve satisfactory suspension of cocoa in milk. This minimum amount ranges, with the different commercial products sold in this country, from 0.04% to 0.08% on the weight of milk. Carrageenin solutions are relatively viscous but the concentrations required to stabilize chocolate milk do not increase the viscosity of aqueous solutions sufficiently to explain suspension by Stoke's law. It appears that the high suspending power of carrageenin can be explained only by postulating a reaction between the carrageenin and one or more of the other components of the system.

Many such reactions are conceivable but the possibility that carrageenin enhances the viscosity *of milk* far more than it increases the viscosity *of aqueous solutions* was examined first. Other studies were undertaken to determine the nature of suspension and to correlate suspending power and other physical properties of carrageenin.

Little has been published on physical properties of carrageenin. Salts, particularly potassium salts, enhanced the gelling properties of carrageenin solutions (5, 9). The viscosities of cold water extracts of *Chondrus crispus* have been studied (1, 4) but other work has shown that cold water extracts differ from hot water extracts (5) which are used commercially. The viscosity of carrageenin solutions was decreased by salts (10) and this was explained in terms of decreased solubility, but a more probable explanation is that carrageenin solutions exhibit electroviscous effects and are sensitive to traces of salt.

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[2] *Biochemist.*
[3] *Director.*

Little relation was found between suspending power and the viscosity of 2% solutions at 60°C., or the gold number, or certain other properties (7). The amount of calcium oxalate held in suspension by carrageenin under specific conditions was related to suspending power, but salts affected the results (11). Moreover, colloids often prevent crystal growth and as the calcium oxalate was precipitated in situ the prevention of sedimentation may have been due largely to this effect and not to the suspension of particles of the size of powdered cocoa.

Materials

Some samples of carrageenin were laboratory prepared by a procedure described elsewhere (7), others were commercial samples supplied by the Kraft Foods Company and by the Krim-Ko Company. All samples contained salts; salt-free samples were prepared, when needed, by extracting carrageenin with 60% alcohol (by volume) until free from chlorides, then pressing and air drying.

Suspending Power a Function of Viscosity

Methods and Incidental Studies

Solutions of carrageenin were prepared by dispersing carrageenin in milk at 70°C., and holding the mixture, with occasional shaking, in a bath at this temperature for 20 min. They were then cooled rapidly with gentle swirling to 10°C., and stored at 5 to 10°C. for 24 hr. Viscosities were determined in A.S.T.M. Standard, Size 100, Fenske Modified Ostwald Viscometers. Ostwald viscometers are not ideal for thixotropic solutions (such as those encountered in this study) but they have practical advantages. The upper bulbs of the Fenske type of viscometei are filled without running the liquid through the capillary.

Tests showed that concentrations of carrageenin similar to those required to stabilize chocolate milk greatly increased the viscosity of milk and that slightly higher concentrations resulted in the formation of distinct but weak gels. Some difficulty was found in obtaining reproducible viscosities. The milk varied from day to day, so the same milk was used throughout any series. Running the solution through the viscometer reduced the viscosity, therefore the first flow time was recorded; to repeat a reading the viscometer was emptied and refilled with fresh solution. When the solutions containing carrageenin were held at 25°C. their viscosities dropped slowly, consequently a standard warming up time had to be adopted—five minutes was chosen. At 10°C. this warming up problem did not arise and this temperature was used for some of the later measurements. The viscosities of several 0.04 to 0.07% solutions were approximately twice as high at 10°C. as when warmed to 25°C.

A brief study showed that the viscosity developed rapidly in cold milk; immediately after cooling from 70°C. to 10°C., the viscosity of a 0.06% solution of Sample 5 (suspending concentration 0.06%) was 80% of its viscosity

after 24 hr. refrigeration. This is a high initial viscosity, in view of the fact that the solutions are thixotropic and had been swirled during cooling.

The addition of 2% cocoa and 3% sugar, as used in chocolate milk, increased the viscosity of milk and of solutions containing little carrageenin but had no effect on the viscosity of milk containing enough carrageenin to suspend the cocoa. Thus, for 0.05% and 0.06% solutions of Sample 5 (suspending concentration 0.06%), the viscosity at 25°C. in milk was 6.1 and 8.3 centistokes respectively and in chocolate milk it was 6.2 and 8.2 centistokes respectively. Consequently, sugar and cocoa were not included in the main series of viscosity studies.

Chocolate milk suspensions were prepared in the same way as carrageenin solutions, with 2% cocoa (passing 80 mesh) and 3% sugar in addition to the carrageenin and milk. Carrageenin concentrations were chosen at 0.005% increments, e.g., 0.040%, 0.045%, etc. The suspensions were mixed by shaking in stoppered flasks and the mixtures were strained through an 80 mesh sieve prior to refrigerating. Sedimentation was determined visually after storing the mixtures for 24 hr. at 5° to 10°C. The minimum concentration required to stop sedimentation was taken as the suspending concentration, and the reciprocal of this is referred to as the suspending power. Since the determinations were visual and were made at definite concentration increments, the values for suspending concentration are only approximate.

Effects of Carrageenin on the Viscosity of Milk

Fig. 1 shows viscosity concentration curves for five samples of carrageenin in milk. For Sample 1, measurements above 0.04% are not given because above this concentration the milk separated into curd and whey and the viscosity of a 0.045% solution was less than that of a 0.04% solution. Similarly, for Sample 2 the viscosity of a 0.055% solution was less than that of a 0.05% solution.

These curves are all similar in shape and can be made to coincide by selecting a suitable horizontal scale for each one. Thus if the scales for Samples 2, 3, 4, and 5 are divided by the factors 1.12, 1.20, 1.28, and 1.45 respectively the curves all coincide with that for Sample 1. These factors represent the relative concentrations needed to reach a specified viscosity, such as 4, 6, or 8 centistokes. They are referred to in this paper as "relative concentration factors" and the relation among curves as the "relative concentration relation". No special significance is attached to Sample 1 and any of the curves could have been selected as a reference. The factor for an additional sample can be determined by measuring the viscosity of one concentration, say 0.03%, and dividing that concentration by the concentration of the reference sample at the same viscosity. Multiplying the concentration of the reference sample at a selected viscosity by this factor gives the concentration of the additional sample needed to give the same viscosity.

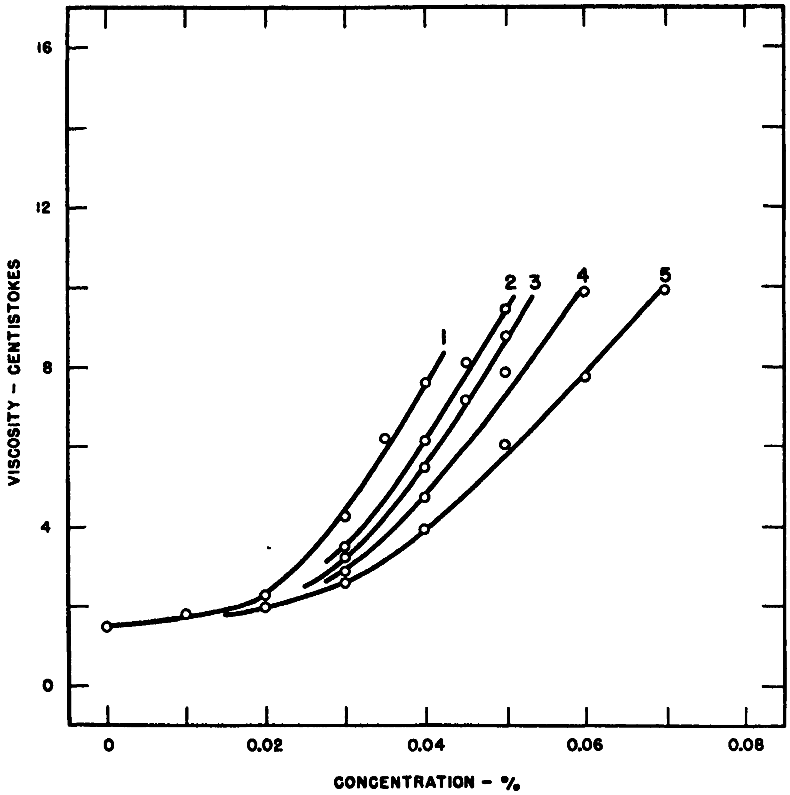

FIG. 1. *Effect of concentration on the viscosity at 25° C. of carrageenin in milk.*

Relation Between Viscosity in Milk and Suspending Power

For these samples, the suspending concentration was closely related to the amount of each required to increase the viscosity of milk, as measured in this study, to 7.5 centistokes at 25°C., i.e., 15 centistokes at 10°C. To investigate this relation more thoroughly, the suspending concentrations of 16 additional samples were determined and compared with the amount of each required to increase the viscosity of milk to 7.5 centistokes at 25°C. The latter values were calculated from the measured viscosity of duplicate 0.03% solutions of each sample in milk by applying the method given in the foregoing section. A 0.03% concentration of carrageenin was chosen as it gave a good viscosity spread among the samples and the results were more reproducible than those for higher concentrations, which may produce curd and whey.

Fig. 2 shows the results for the 21 samples and the correlation coefficient was .98. The magnitude of this coefficient suggests that stabilizing chocolate milk is a matter of increasing the viscosity to a point where cocoa does not settle.

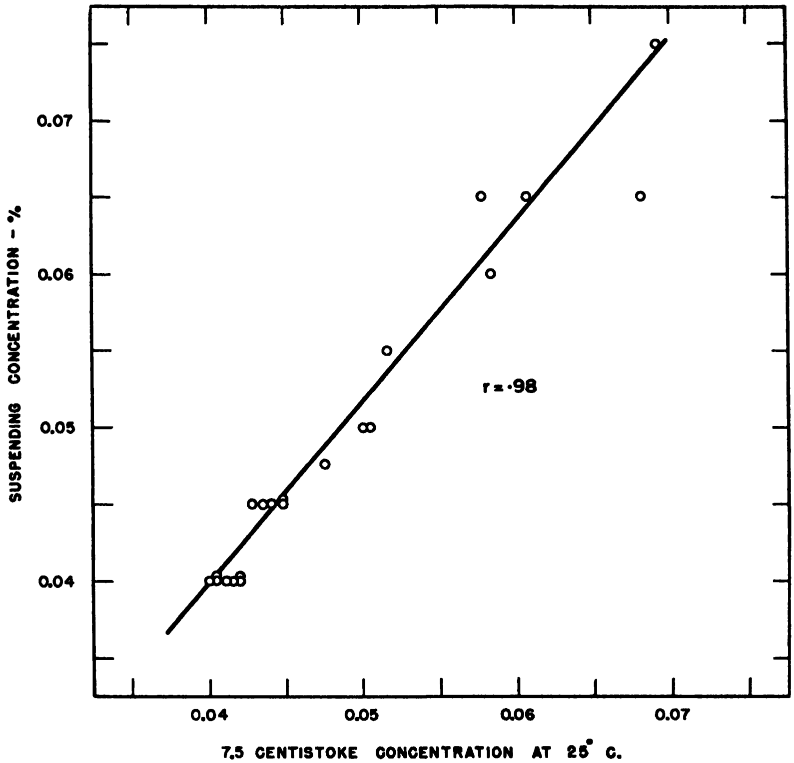

FIG. 2. *Relation between suspending concentration and concentration of solutions with viscosities of 7.5 centistokes at 25° C.*

Stabilization of Other Systems

If the foregoing is correct it should be possible to stabilize other systems by increasing their viscosities. To investigate this, systems were studied in which the components of chocolate milk were eliminated singly. The methods followed were the same as those used in preparing and studying chocolate milk; care was taken to keep the pigment in suspension until the solutions thickened.

In the first series, pigments other than cocoa were used. Preliminary observations showed that of a calcium carbonate, a talc, a kaolin, and a carbon black, only the last had approximately the same sedimentation rate as cocoa in milk; 2% carbon black on the weight of milk was used. In the second series a low viscosity sodium alginate (obtained from Alginate Industries Ltd., London, England) was used in place of carrageenin. Sodium alginate does not dissolve readily in milk; concentrated aqueous solutions were prepared and one part used to nine of hot milk. Alginate thickens milk because the calcium in milk converts it to calcium alginate, which is a gel under these conditions. In the third series 0.04 N potassium chloride solutions were used in place of milk. Difficulty was experienced in detecting sedimentation in this medium.

In milk, settled particles of cocoa are seen against a whitish background but in aqueous media the background is the same color as the cocoa. This difficulty was diminished by lowering a Lucite rod, with a light at the top, into the medium. Particles could be seen against this light; sedimented particles could be pushed together with the Lucite rod.

The minimum concentration of suspending agents and the viscosities of the stabilized systems are given in Table I. Viscosity is particularly sensitive to concentration in this region, but suspending concentrations cannot be determined accurately; therefore, these values (14 to 17 centistokes) are considered to be in good agreement. As high viscosity was the one factor common to all four systems, these results support the view that stabilization is a matter of high viscosity.

TABLE I

VISCOSITY OF STABILIZED SYSTEMS AT 10°C.

System	Minimum suspending concentration, %	Viscosity of stabilized system, centistokes
Milk–carrageenin–cocoa	0.040	15.0
Milk–carrageenin–carbon black	0.040	15.2
Milk–sodium alginate–cocoa	0.175	17.1
0.04 *N* KCl–carrageenin–cocoa	0.225	14.2

The Casein Complex and Carrageenin

Although the foregoing indicates that viscosity is important in stabilization, no clue is given as to the components of milk that contribute to the viscosity increases on the addition of carrageenin; various relations were therefore studied.

Effects of Milk Components on the Viscosity of Carrageenin Solutions

Sample 1 (suspending concentration 0.04%) was used throughout and measurements were made of the viscosity of solutions in the following: milk, skim milk, milk dialyzed for four days against 0.05 *N* sodium chloride at 5°C. in viscose tubes, whey (from rennet coagulated milk), 2.8% casein at pH 6.8 in 0.04 *N* potassium chloride, salt solutions whose concentrations approximated that of the various cations in milk (2, p. 294), and 0.05 *N* sodium chloride. The casein had been prepared by acid precipitation at the isoelectric point. All solutions were refrigerated for 24 hr. and the viscosity was calculated from the first flow time through the viscometer.

In Fig. 3, the viscosity at 25°C. was plotted against the concentration of carrageenin. These results show that skim milk is not appreciably different from whole milk, as only slightly more carrageenin was needed to bring the viscosity to the 7.5 centistoke or suspending level. Whey required a concentration of 0.22%, or five times as much, to reach the 7.5 centistoke level; in fact, whey is no better than 0.04 N potassium chloride, a concentration that

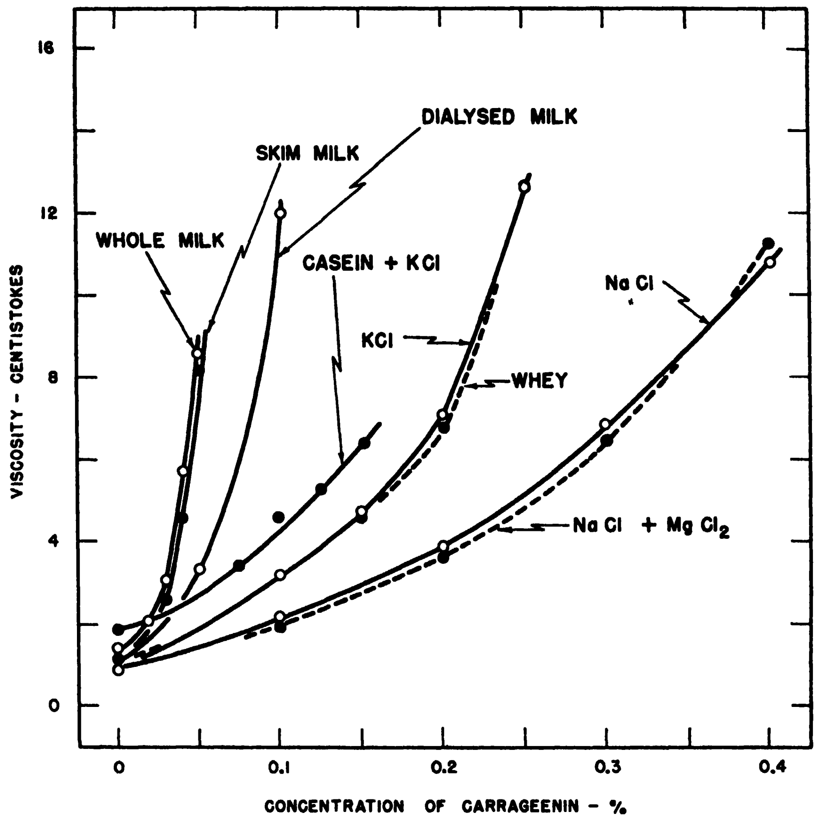

FIG. 3 *Effect of carrageenin on the viscosity at 25°C. of milk and milk components.*

was selected because milk contains about this amount of potassium ions (2, p. 294). The curves for solutions in 0.05 N sodium chloride and in 0.025 N sodium chloride plus 0.015 N magnesium chloride were similar. The addition of 0.06 N calcium chloride to 0.04 N potassium chloride caused the mixture to separate into two phases and viscosity measurements were meaningless.

The curve for dialyzed milk shows that dialyzing, which probably removed potassium, calcium, and phosphate ions, approximately doubled the amount of carrageenin required to reach the 7.5 centistoke level. Adding potassium chloride to dialyzed milk had no effect. Adding calcium chloride caused the milk to coagulate and it could not be studied.

The curve for casein plus potassium chloride had to be discontinued at 0.15% carrageenin; above this concentration the mixture separated into two phases. The results show that the casein solution did not behave in the same way as milk.

These results show that, with the exception of the removal of fat, modifications of the milk increased the amount of carrageenin needed to reach the 7.5 centistoke level. This suggests that the natural casein-complex present in milk is responsible for the large increase in viscosity of milk on the addition of small amounts of carrageenin. If this complex is upset by dialysis or by removing the casein, much more carrageenin is required to build up the viscosity.

Gelling of Milk with Carrageenin

The most probable explanation of these observations is that carrageenin and the casein-complex gel together. Definite evidence of this was obtained by adding 0.1% of Sample 1 to milk. This set to a gel, which on refrigerating and stirring separated into curd and whey, indistinguishable from rennet curd and whey. An analysis of the whey from the carrageenin-coagulated milk showed it to contain 1.52 mgm. of nitrogen per ml., as compared with 1.42 mgm. of nitrogen per ml. of whey from rennet-coagulated milk. The addition of hydrochloric acid to the whey from carrageenin-coagulated milk did not give a precipitate. These observations suggest that carrageenin effectively precipitated the casein. The casein–carrageenin gel melted when warmed to 40°C., which is in the region of the temperature at which aqueous gels melt.

Relation Between Suspending Power in Milk and Viscosity in 0.05 *N* Sodium Chloride

Although the foregoing helps to elucidate the mechanism of chocolate milk stabilization it does nothing to explain the difference between carrageenin of high and low suspending powers. As mentioned previously, aqueous solutions of carrageenin are relatively viscous and an obvious choice of investigations was to examine any relation between the viscosity of carrageenin in aqueous solutions and in milk. Before this could be undertaken it was necessary to study the effect of other factors on the viscosity of aqueous carrageenin solutions.

Methods

Aqueous carrageenin solutions were prepared by dispersing carrageenin in boiling water and holding the mixture, with occasional shaking, in a hot water bath for 20 min. The heating time was not critical from the standpoint of viscosity—a solution was heated for an additional 20 min. without reducing its viscosity significantly. For a series of solutions, a stock solution was prepared and diluted by weight with water, salt solution, or buffer, as required, and then heated to 50°C. and cooled again to 25°C. Viscosities were determined in A.S.T.M. Standard, Size 100, Fenske Modified Ostwald Viscometers. pH was determined electrometrically.

Effects of Salts, pH, Storage Temperature, and Concentration

As would be expected these four factors are interrelated. Fig. 4 shows the effects of sodium chloride and of calcium chloride on the viscosity at 25°C. of solutions of 0.1% salt-free, air-dry carrageenin. Curves for magnesium chloride and lithium chloride were similar to those in Fig. 4. It is evident from the shape of these curves that carrageenin exhibits the well known electroviscous

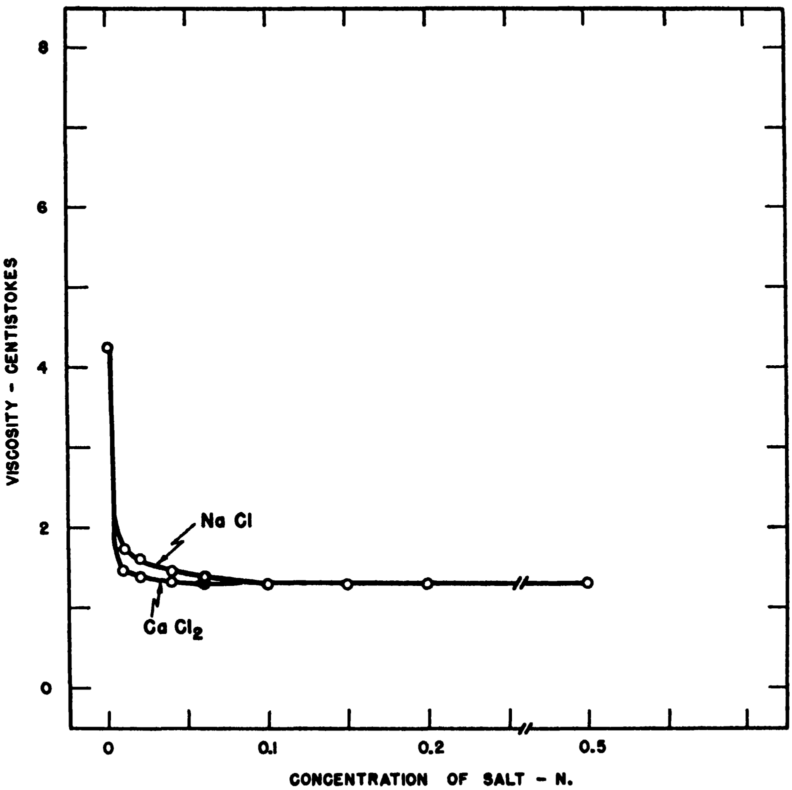

FIG 4 *Effect of salts on the viscosity at 25°C of 0 1% carrageenin solutions*

effect (6, p. 171). The viscosities of these solutions did not alter over a period of three days at 25°C. Potassium chloride in concentrations up to 0.05 *N* had the same effect as sodium chloride on the viscosity of 0.1% carrageenin solutions stored at 25°C. but greater amounts of potassium chloride promoted gelling. At 60°C., which is above the gelling temperature of carrageenin, the viscosity of 0.1% carrageenin solution in water was 1.9 centistokes, in 0.1 *N* sodium chloride it was 0.73 centistokes, and in 0.1 *N* potassium chloride it was 0.75 centistokes.

Table II shows the effects of pH on the viscosity of 0.1% carrageenin solutions in 0.1 *N* sodium chloride, after storage at 25°C. for periods up to one week. The solutions were prepared in 0.1 *N* sodium chloride because preliminary tests

TABLE II

EFFECT OF pH ON VISCOSITY OF 0.1% CARRAGEENIN (IN 0.1 N SODIUM CHLORIDE) STORED AT 25°C.

pH	Viscosity at 25°C., centistokes		
	After ½ hr.	After 1 day	After 1 week
1 2	1 32	1 03	0.96
3 7	1.36	1.35	1 30
4 4–8.8	1 35	1 34	1 34
12 2	1 31	1.27	1 24

showed that some of the buffers (acetic and boric acid) did not swamp the electroviscous effect. The pH was adjusted by adding 0.1 N hydrochloric acid; 0.1 N mono- and disodium phosphate; 0.2 M boric acid and sodium borate; and 0.1 N sodium hydroxide. The results indicate that hydrogen ion concentration had no appreciable effect except at the extremes, where it probably promotes depolymerization.

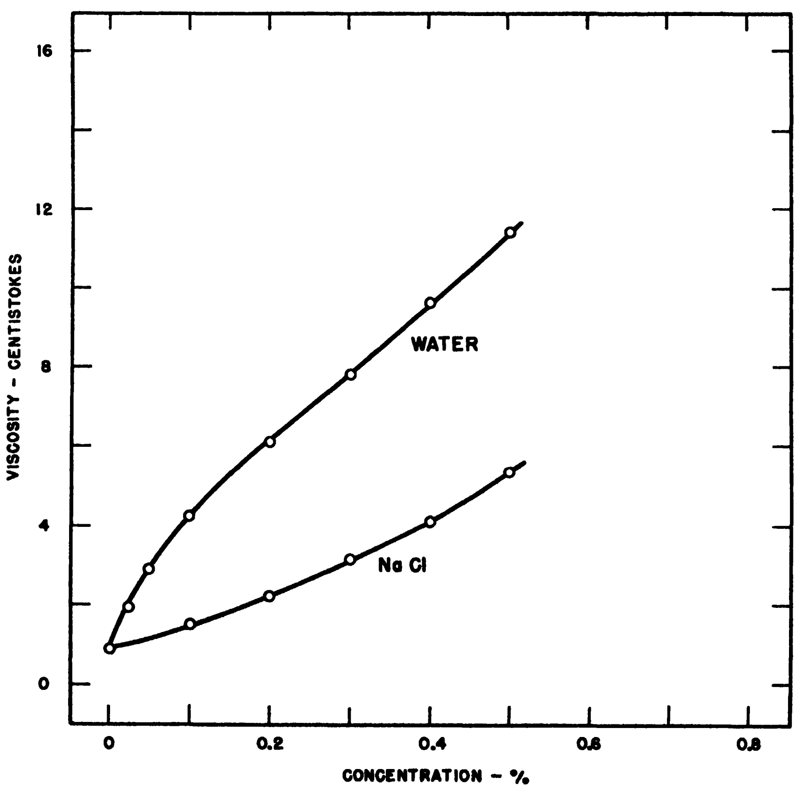

FIG. 5. *Effect of concentration and salt on the viscosity at 25°C. of carrageenin solutions.*

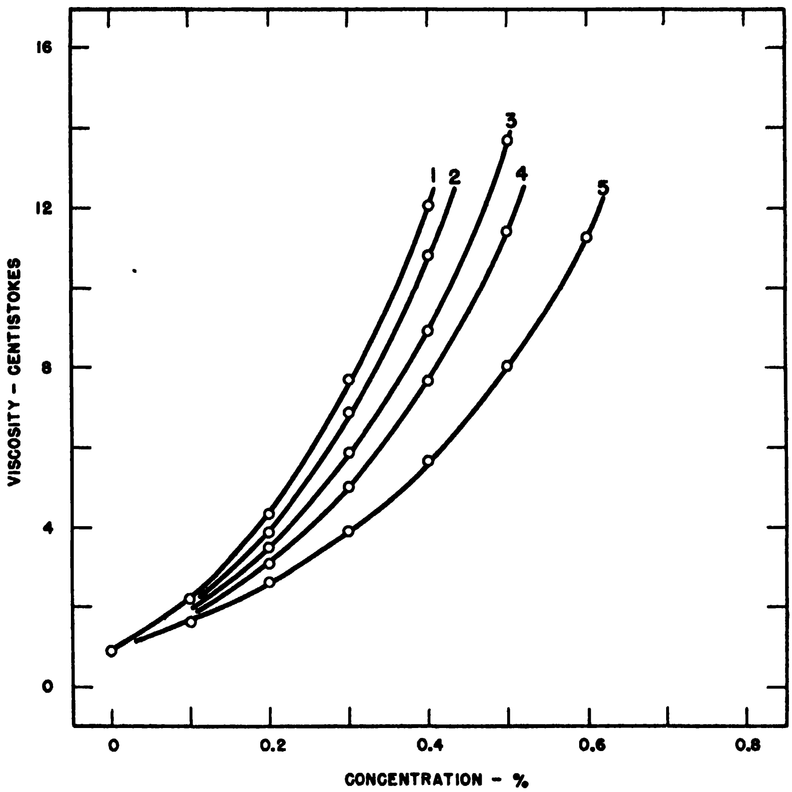

FIG. 6 *Effect of concentration on the viscosity at 25°C of carrageenin in 0.05 N sodium chloride*

Storage at 10°C. increased the viscosities at 25°C of many carrageenin solutions. This is undoubtedly associated with gelling and may be attributed to aggregation of carrageenin. Salt-free carrageenin gels melted between 35°C. and 40°C. but solutions did not gel unless held at a lower temperature for some time. Gels containing potassium chloride melted between 55°C. and 60°C. Salts that enhanced gelling increased the effect of cold storage on viscosity. A method of avoiding these hysteresis effects is to determine the viscosity at 60°C.

Fig. 5 shows the relation between the concentration of carrageenin and the viscosity of solutions in water and in 0.05 *N* sodium chloride. None of the solutions had been cooled below 25°C. With low concentrations of carrageenin in water, the viscosity increment decreased with increasing concentration. This is attributed to the autoswamping of the electroviscous effect by the carrageenin itself as its concentration increased.

Fig. 6 shows the viscosity–concentration curves for a number of different samples of carrageenin in 0.05 *N* sodium chloride. This salt concentration was chosen as it effectively swamped the electroviscous effect but was insufficient to promote gelling in these concentrations of carrageenin at 25°C. These

curves are all similar in shape and the "relative concentration relation" discussed previously holds. If Sample 1 is taken as the reference the "relative concentration factors" for Samples 2, 3, 4, and 5 are 1.08, 1.21, 1.33, and 1.60 respectively. The factors for additional samples, and the concentration needed to give a specified viscosity within the range studied, can be determined as discussed previously.

Viscosity and Suspending Power

Fig. 7 shows the relation between the relative concentration factors for 21 samples of carrageenin in 0.05 *N* sodium chloride and their suspending concentrations for cocoa in milk; the correlation coefficient was .91. The factors

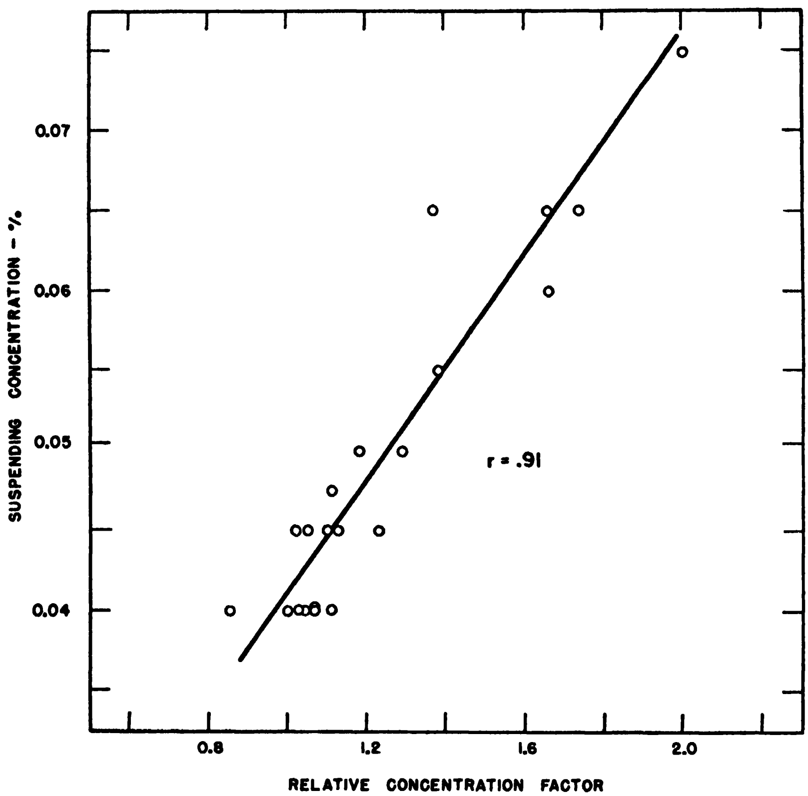

FIG. 7. *Relation between suspending concentration and "relative concentration factor" in 0.05 N sodium chloride.*

were calculated, as previously described, from the viscosity of duplicate 0.2% solutions. A correlation coefficient of .89 was found between the relative concentration factors in milk and the relative concentration factors in 0.05 *N* sodium chloride.

The magnitude of these correlation coefficients does not eliminate the possibility that the difference between samples of high and of low suspending

power is due to impurities. An inert diluent in carrageenin would increase its relative concentration factors in both milk and 0.05 *N* sodium chloride proportionately and would not, therefore, affect the relation between them. Potassium salts may enhance viscosity, but a brief study showed that mixing potassium chloride with carrageenin increased its relative concentration factors in both milk and 0.05 *N* sodium chloride in proportion to the amount of potassium chloride added. (The relative concentration factors were calculated from the viscosities at 25°C. of refrigerated 0.03% solutions of the mixtures in milk and freshly prepared 0.2% solutions in 0.05 *N* sodium chloride.) Potassium chloride under these conditions was therefore acting as a diluent.

Extracting a sample of low suspending power with alcohol–water solutions did not increase its suspending power. Storing a sample of high suspending power at 60°C. for 30 days increased its suspending concentration from 0.04% to 0.05%, its 7.5 centistoke concentration in milk from 0.04% to 0.05% and its relative concentration factor in 0.05 *N* sodium chloride from 1.0 to 1.3. These relative increases are similar but in the absence of tests for purity this does not prove that low suspending power is not due to an impurity: the alcohol–water extraction given might not remove impurities and the heat treatment given here and elsewhere (7) could conceivably have modified a portion of the carrageenin so that it constituted an impurity. However, the latter is most unlikely and it appears probable that suspending power is related to the molar mass of the carrageenin.

Summary and Discussion

This work shows that the essential factor in suspending cocoa in milk is to increase the viscosity of milk to a point where cocoa does not settle. With the cocoa used this required a viscosity, as measured in this study, of 7.5 centistokes at 25°C., i.e., 15 centistokes at 10°C. and, since the chocolate milk was stored at the lower temperature, it was the 15 centistoke level that prevented sedimentation. Viscosities were measured at medium rates of shear; at very low rates, such as those caused by slowly settling cocoa particles, the viscosities would be higher. Consequently, the true stabilizing viscosity would be more than 15 centistokes at 10°C. For different samples of carrageenin the correlation coefficient between the suspending concentration and the concentration needed to raise the viscosity of milk to the 7.5 centistoke level was .98. Tests in which the components of chocolate milk (cocoa, carrageenin, and milk) were replaced singly by carbon black, sodium alginate, and 0.04 *N* potassium chloride, respectively, showed that each of the components could be eliminated without upsetting the stability of the system, provided the viscosity was maintained at approximately 15 centistokes or higher.

The results also indicate that the high viscosity of milk containing carrageenin is due to the formation of a casein–carrageenin gel. This gel melts at about the same temperature as an aqueous carrageenin gel, which suggests that the main structure is due to carrageenin. This is supported by the rela-

tion between the viscosity of carrageenin in aqueous solutions and its suspending power. Carrageenin is probably a polymer of a metal-organic-sulphate, linked through the organic part (3), but the gelling of milk with carrageenin is not similar to the precipitation of proteins with detergents, such as sodium dodecyl sulphate, as they precipitate only below the isoelectric point(8).

Probably the carrageenin forms a weak gel into which the casein-complex fits and which it fortifies. It is interesting to compare carrageenin gelling of milk with rennet gelling or coagulation; in the latter the rennet upsets the casein-complex so that it forms an irreversible gel, whereas the former apparently forms a heat reversible gel. The action of carrageenin on the casein-complex may be of use in studying casein.

Finally, suspending power in milk was related to the viscosity of carrageenin in aqueous solutions, and, although this is not in itself proof, it indicates that suspending power is related to the mean molar mass of the carrageenin. This is receiving further study.

From a practical standpoint this work suggests that viscosity of milk containing carrageenin is a reliable measure of its suspending power since the correlation coefficient between them was .98. However, milk itself is variable and unstable and is not an ideal medium for comparative tests. Consequently, viscosity in 0.05 N sodium chloride, although the correlation coefficient between this and suspending power was lower (.91), would probably be a more convenient measure of suspending power. Viscosity in 0.05 N sodium chloride also has the advantage that it can be measured immediately after the solutions are prepared, whereas solutions in milk must be refrigerated for a standard time prior to viscosity determinations.

Acknowledgments

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

X. THE CAUSE OF PREIGNITION (SURFACE IGNITION)—UNDOPED LIQUID FUEL[1]

BY R. O. KING[2] AND E. J. DURAND[3]

Abstract

The theory is advanced that surface ignition, generally described as preignition, if occurring during compression, is due to partial oxidation of the fuel to aldehyde, a relatively small concentration of this inflammable substance being sufficient for ignition of the charge by the hot surfaces normally present in the combustion space of a high duty engine. The igniting effect may be early or late, that is, before or after spark ignition. Early surface ignition may cause destruction of pistons and exhaust valves of supercharged engines and is indicated by severe knocking. When the effect occurs late in the combustion period there is no destructive effect and the engine will run without spark ignition. The theory is confirmed by engine experiments with rich mixtures which oxidize readily to aldehyde, and it is shown that the occurrence of surface ignition then depends on surface and mixture temperatures. Thus in temperature conditions chosen to eliminate surface ignition, *n*-heptane can be used in the C.F.R. engine at 10 : 1 compression ratio and the performance of acetaldehyde does not differ from that of a hydrocarbon fuel. A conclusion of importance in practice is that early surface ignition may occur in a particular cylinder of a multicylinder supercharged engine receiving an extremely rich mixture, because of uneven distribution. If the surface ignition led to the destruction of an exhaust valve or a piston, continued running of a highly supercharged engine on the unaffected cylinders would have the disastrous consequences arising from explosion of the compressed mixture in the induction system.

Introduction

An essential condition of the type of knocking combustion frequently described as "detonation" is that the end gas be in a chemical or physical state such that flame propagation can occur in it at an abnormally high rate, otherwise combustion, already proceeding at normal velocity, would be completed without knock. It is held generally that the presensitization of the end gas is due to preflame oxidation reactions. On the other hand, according to the hypothesis advanced in Part IV (10), an abnormally high rate of flame propagation is a consequence of the end gas having become impregnated with finely divided carbon. The carbon is provided by pyrolysis of the lubricating oil when hydrogen or town gas is used as engine fuel, as demonstrated experimentally, Parts V (13) and VI (14), but mainly by pyrolysis of the fuel when liquid hydrocarbons are used.

Abnormally rapid combustion of the presensitized end gas might occur by sudden acceleration of the normal rate of flame movement as in long tubes; in the

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Contribution from Defence Research Board, Ottawa, Canada, in association with the Department of Mechanical Engineering, University of Toronto.

[2] *Research Scientist, Naval Division, Defence Research Board and Honorary Lecturer, Department of Mechanical Engineering, University of Toronto. Lately Director of Scientific Research and Development, Royal Canadian Navy.*
[3] *Lecturer, Mechanical Engineering, University of Toronto.*

engine combustion space the effect can be initiated by nuclei acting as promoters of ignition or by the igniting effect of hot surfaces Both types of ignition are shown by the high speed photographs of knocking combustion taken by Withrow and Rassweiler (21) The phenomena are shown even more distinctly by the ultra high speed photographs taken by Miller (17) and by Miller, Olsen, Logan, and Osterstrom (18).

Surface ignition, unlike the nuclear type, need not be confined to the end gas and may occur at any time after the opening of the inlet valve and is described loosely as preignition The term would better be applied to induction ignition which seldom occurs unless initiated by the residual flame of slow burning mixtures The term "surface ignition" is therefore applied to an igniting effect arising after the closing of the inlet valve

When surface ignition occurs before optimum ignition timing, it is equivalent to advancing the spark and will be described as "early" When it occurs after optimum ignition timing, it is equivalent to retarding the spark and will be described as "late" The engine will continue to run on late surface ignition when spark ignition is switched off

"Preignition" is commonly believed to be due to the igniting effect of incandescent spark plug points or patches of carbonaceous or other matter in respect of the combustible mixture as admitted to the engine cylinder Induction ignition is possible accordingly but not the surface ignition which occurs especially when using rich mixtures after the inlet valve closes and the "hot points" have been cooled by the entering charge Incidentally, methanol is exceptionally prone to surface ignition in spite of the cooling effect due to the high latent heat of vaporization Thus an increase in the inflammability of the combustible mixture during compression in combination with suitable temperatures appeared to be required for promotion of surface ignition

An increase of inflammability would be obtained on the partial oxidation of the hydrocarbon fuel to aldehyde which is known to occur during compression, and whether or not ignition then occurred would depend on the concentration of aldehyde attained and on maximum surface temperature which can be controlled, especially in a liquid cooled engine The engine experiments to be described were planned accordingly, it being assumed as indicated by the experiments of Part II (8) that aldehyde is formed by a heterogeneous oxidation reaction and that ignition of the substance is not autocatalytic

Experimental Arrangements

The standard C F R engine was used for the experiments Richer mixtures than usual were obtained as required by using oversize fuel flow control orifices Knock intensity described as "standard" is defined in Part VIII (12, p. 215) and is somewhat lighter than the A S T M standard.

The fuels used for the experiments were as follows,—

Fuel S, Lot 1: Distillation range 85° to 429°F. See graph of Fig. 1, Part VIII (12), for details.

n-Pentane: technical grade, initial boiling point 94°F., dry point 100°F.

n-Hexane: commercial grade, initial boiling point 150°F., dry point 156°F.

n-Heptane: as supplied for octane number determination according to C.F.R.-A S.T.M. procedures; boiling point closely approximates the correct value of 98.38°C. (209°F).

Acetaldehyde: pure, boiling point, 21°C. (70.8°F.).

Preliminary Engine Experiments with the Three Paraffins and Fuel *S*

Temperatures of initial oxidation or combustion of pentane, hexane, and heptane taken as indicated by the appearance of peroxides, aldehyde, water,

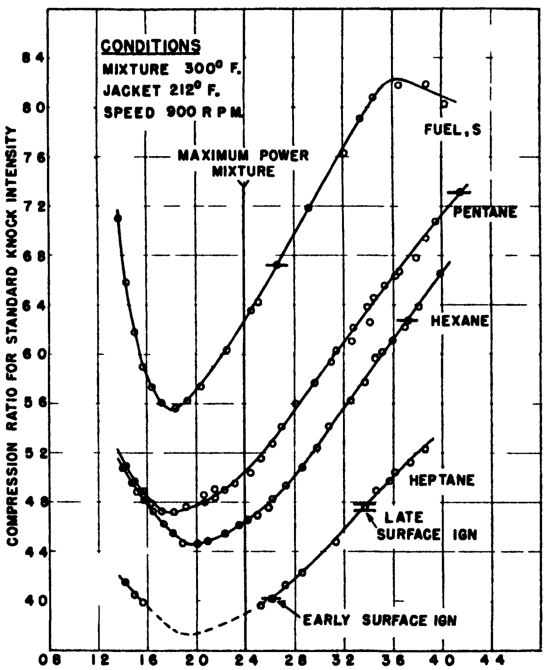

FIG 1. *Effect of mixture enrichment on the combustion of heptane, hexane, pentane and fuel S in the engine*

and carbon oxides in the reaction products, are given by Pye (20, p. 98) as 295°, 266°, and 230°C. respectively. The given values are regarded as approximate only, mixture strength not having been closely controlled.

Preliminary engine experiments using the three paraffins mentioned and fuel *S* were made in high temperature operating conditions, mixture strength

being continuously enriched to promote surface ignition while compression ratio was increased to maintain standard knock intensity. Ignition timing was retarded as compression ratio was increased, in accordance with the C.F.R.–A.S.T.M. method of knock rating. The results of the experiments are given by the graphs of Fig. 1.

The beginning of early surface ignition is marked on the graphs by single short horizontal lines. It will be noted, as would be expected from the consideration mentioned above, that the effect occurred at decreasing mixture strength and decreasing temperature as represented by usable compression ratio, as the paraffin series was ascended from pentane to heptane.

Late surface ignition on which the engine would run without spark ignition is indicated by the pair of short horizontal lines on the graph for heptane. The effect was obtained with that fuel only. There were indications of early surface ignition when rates of heptane supply were even lower than those indicated on the graph as marking the beginning of the effect. The occasional surface ignition knock then obtained was "heavy", as would be expected. On the other hand, the late surface ignition knock observed when the engine would run without spark ignition was nearly continuous, and intensity differed so little from that adopted as "standard" that it was necessary to switch off the spark ignition to demonstrate the existence of the effect.

Cool Engine Experiments with Heptane

The preliminary experiments indicated that heptane was the most suitable fuel to use for engine experiments to be made in conditions adapted to eliminate combustion knock due to either early or late surface ignition. Further experiments were made, therefore, with the temperature of the jacket cooling water, taken at the outlet, reduced to 100°F., the heptane–air mixture unheated, and the engine speed reduced to 400 r.p.m. to reduce power and consequently the temperature gradient from the combustion space surface to the coolant. The experimental results are given by Graph *A* of Fig. 2. A second set of experiments was made in similar temperature conditions but with the engine speed raised to 900 r.p.m. The results are given by Graph *B* of the figure. Graph *C* of the figure for the heptane as used in standard C.F.R.–A.S.T.M. knock testing conditions is reproduced from Fig. 1 to show the remarkable change in performance obtained on eliminating surface ignition.

There was not the slightest indication of early or late surface ignition during the low temperature experiments, at either 400 or 900 r.p.m. At 400 r.p.m. standard knock intensity could be maintained at compression ratios rising from 4.55 to 10:1 as the rate of heptane supply was increased from 1.3 to 2.1 lb. per hr., which represents an increase in mixture strength of 62%. At 900 r.p.m. standard knock intensity could be maintained as compression ratio was raised from the minimum value of 5.3 to the measurement limit of 10, on increasing mixture strength by 50% only. It should be noted that the minimum

value of usable compression ratio is usually obtained at the "correct" mixture strength and that an increase of as much as 30% may be required to obtain maximum power.

The fuel performance obtained on the elimination of surface ignition is believed to be that governed by nuclear ignition of the end gas, and the de-

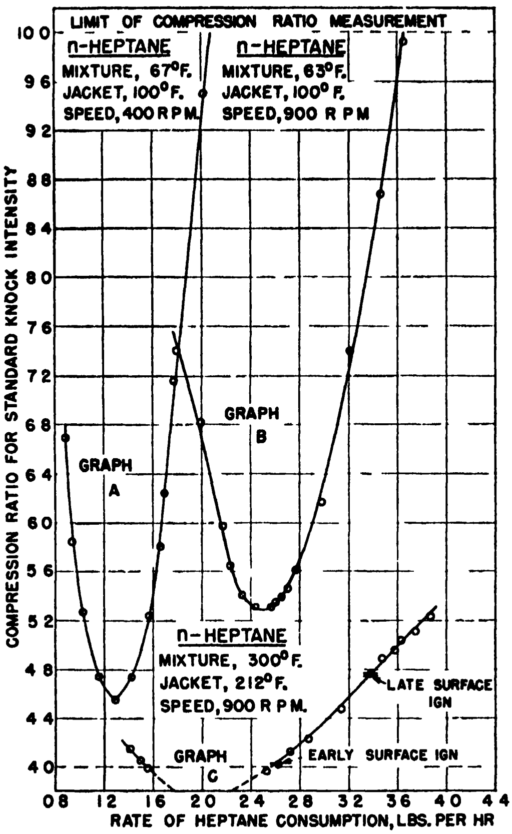

FIG 2 *Effects of surface temperature and enrichment of the mixture on the combustion of heptane in the engine*

crease of knock with increase of engine speed can then be attributed to the consequent decrease in the time available for pyrolysis of the fuel to yield the required concentration of finely divided carbon.

Engine Experiments with Acetaldehyde

Prettre (see W. Jost (7, p. 441)), discussing the luminescence of heated acetaldehyde-air mixtures, mentions that the lively combustion of the mixtures with a small surplus of aldehyde assumes an explosive form that is never observed in hydrocarbon-air mixtures and that normal ignition takes place at about 350°C. Egerton and Gates (2) obtained an igniting temperature of

395°C. on allowing a drop of acetaldehyde to fall into a heated iron pot; the igniting temperature of pentane was 515°C. in the same circumstances. It would be expected, therefore, that an acetaldehyde–air mixture would ignite prematurely if used in an engine as usually operated. Thus Egerton, Smith, and Ubbelohde (3, p. 464) state that the pure substance, b.p. 21°C., when used as fuel for an ethyl knock testing engine was "found to knock so violently that the engine could not be run".

It seemed to be possible, in the light of the experiments made with heptane, that the violent knock observed by Egerton *et al.* was due to early surface ignition and ***not*** to explosive combustion of the unburned mixture ahead of the flame, late in the combustion period.

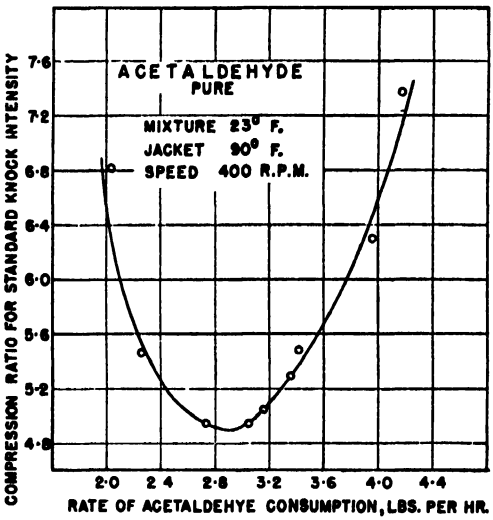

FIG. 3. *The antiknock effect of mixture enrichment when pure acetaldehyde is used as fuel for the C.F.R. engine.*

Experiments with the C.F.R. engine were carried out accordingly in conditions chosen to avoid surface ignition. The jacket cooling water was maintained at 90°F. and the engine run at 400 r.p.m. Furthermore, the experiments were delayed until mid-winter, when it was possible to reduce the laboratory air temperature to 55°F. The quantity of acetaldehyde available for the experiments was insufficient for a determination of the change of optimum ignition timing with change of compression ratio. A fixed ignition advance of 10° was chosen as suitable for a fast burning fuel.

The results of the engine trial are given graphically by Fig. 3. It will be seen that the acetaldehyde behaved like an ordinary hydrocarbon fuel. The minimum compression ratio, 4.9:1, with standard knock intensity was obtained when the rate of aldehyde supply was 2.9 lb. per hr. and standard knock intensity was maintained as rate of supply was increased until compression ratio

reached 7.4:1. The increase of mixture strength was then 48%, the rate of supply of 2.9 lb. per hr. being taken as corresponding to the "correct" mixture strength. The experiment was stopped at the compression ratio of 7.4:1 because frost then affected the flow from the carburetor jet; otherwise it might have been continued until the compression ratio reached the measurement limit of 10:1.

Discussion

The results of the engine experiments accord with the theory that ignition of liquid fuel during compression does not occur until the fuel has been partially oxidized to aldehyde. The results of laboratory experiments described in earlier Parts support the theory.

Thus it was shown by experiments, Part II (8), that pentane ignition temperatures as low as 515°C. and initial oxidation temperatures as low as 295°C. mentioned earlier can be obtained solely if experimental conditions are such that partial oxidation to aldehyde can occur. Turbulence was found to be the essential condition. Oxidation proceeded very slowly without that factor. Reaction was then to steam and carbon dioxide only and, in the absence of aldehyde, ignition could not be obtained even at 750°C., the limit of the indicating instrument. On the other hand, turbulence provided by convection currents in a vertical combustion tube sufficed to start oxidation at temperatures below 300°C., with profuse formation of aldehyde, Fig. 2, Part II, *loc. cit.*, and explosion occurred when the tube wall attained a temperature of 560°C.

The fuel–air mixture on passing the inlet valve of the engine, necessarily with great velocity, enters the hot cylinder and combustion space in a state of high turbulence, and the formation of aldehyde would be expected. The consequent tendency to surface ignition would not, according to the theory advanced, increase with increase of mixture strength unless rate of aldehyde formation increased accordingly. The combined effect of mixture enrichment and turbulence to increase rate of aldehyde formation was shown by experiments described in Part VII (11) using reaction chamber No. 10. The graphs relating to 25% weak, "correct", and 100% rich mixtures with air have been collected and are shown together, Fig. 4 of this Part. Air was supplied to the reaction chamber at 75 cc. per min. and pentane added as required for the stated mixture strengths. The graphs show that aldehyde is formed over the low temperature range at a rate increasing rapidly with increase of mixture strength. The maximum rate of low temperature oxidation, shown by the height of the "aldehyde hump" increased by more than 100% as mixture strength was increased from 25% weak to 100% rich, approximately the usable range in an engine. The fact that ignition did not occur is attributed to the rate of flow through the reaction chamber of 2.5 cc. volume being sufficiently rapid to remove the aldehyde almost immediately after formation.

There is, however, ample available experimental evidence respecting the formation of aldehyde during the compression of hydrocarbon air mixtures in

engines. Thus, Callendar *et al.* (1, p. 28) demonstrated the formation of aldehyde and peroxide during compression and obtained "auto-ignition and detonation" without spark ignition when using a rich mixture of undecane with air in a Ricardo E 35 engine, the mixture being preheated to 80°C. (176°F.) and the jacket water to the same temperature. Measurements were made later by Egerton, Smith, and Ubbelohde, (3, p. 460) of the aldehyde and

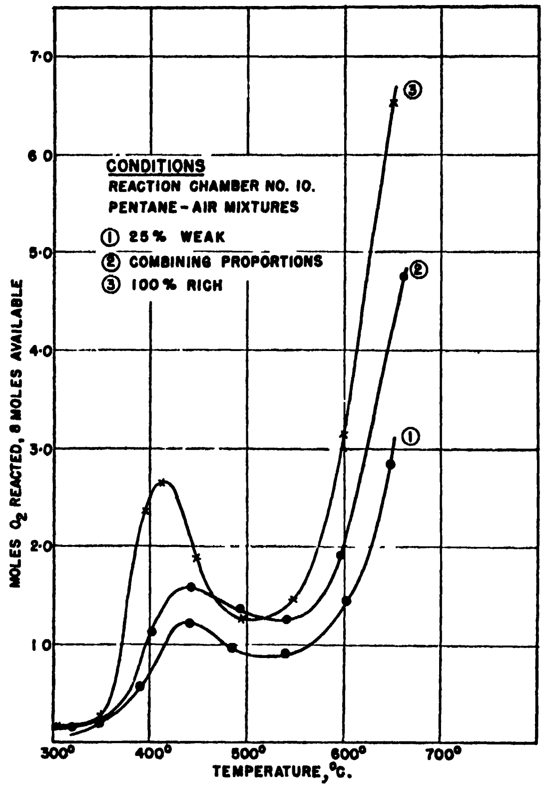

FIG. 4. *Oxidation reaction rates over "low" and "high" temperature ranges as affected by increase of mixture strength.*

peroxide formed during the compression stroke of an ethyl knock testing engine running at 600 r.p.m., using a jacket temperature 212°F. and unheated induction. Aldehyde was formed up to 10% by weight of the fuel although conditions in respect of mixture strength and temperature were not the most favorable. Moreover, although the engine was run under power, samples for aldehyde estimation were drawn only when spark ignition was switched off.

Concluding Comment

The conclusion arising from the experiments described in this Part, namely, that aldehyde is responsible for the preignition or surface ignition that occurs during compression, is novel, so far as known. The widely held view is that

the effect is due to the premature ignition of the fuel–air mixture, ***in the state supplied to the engine***, by exceptionally hot spots in the combustion space such as spark plug points. Temperatures required are, according to Hundere and Bert (6), of the order of 2000°F. (1100°C.) for the first stages of preignition and several hundred degrees higher for very advanced preignition. They conclude that no material in the combustion space can attain the requisite temperatures without melting, other than the ceramic core of the spark plug, certain types of deposits, some from ethyl fluid, because of poor thermal contact with underlying surfaces and in some cases the exhaust valve head. Preigniton occurs frequently, nevertheless, in ordinary motor car engines without surface temperatures rising to the degree required to melt an exhaust valve or an aluminum piston.

The usual method of determining preignition temperature is to heat a "temperature plug" projecting into the combustion space until ignition is obtained in advance of the spark. The extremely high "observed" plug temperature would be required unless the mixture contained excess fuel or constituents prone to oxidize to aldehyde. That is, temperatures of 2000°F. and over must have been observed in conditions in which preignition could not occur normally.

The adverse effect of uneven distribution of fuel–air mixtures to multicylinder engines, in respect of power developed, has long been recognized. Accurate measurements made by Gerrish and Meem (5) show differences in mixture strength as between cylinders of a multicylinder radial aero engine of as much as 30%, and Marble, Ritter, and Miller (16) describe methods of reducing the differences with the object of increasing the possible maximum power.

The experiments described in this Part show that it is important to provide for uniform distribution in order to avoid surface ignition, which, if occurring "early" in one cylinder of a supercharged engine, may have the disastrous consequences following from the burning of the exhaust valves and piston of that cylinder while the engine continues to run on the others.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and Assistant Prof. W. A. Wallace. The cost of the work was defrayed in part by an Extramural Grant from the Defence Research Board (Canada). Assistance was given in the course of the work by Messrs. C. C. Li, E. H. Dudgeon, W. E. Morley, and H. W. M. Mar, all members of the staff of the Department of Mechanical Engineering, University of Toronto, and by Mr. H. Shanfield of the staff of the Department of Chemical Engineering.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XI. THE LOSS OF POWER COINCIDENT WITH THE ANTIKNOCK ACTION OF THE CARBONYLS OF IRON AND NICKEL IN RICH MIXTURES[1]

By R. O. King[2] and Edwin J. Durand[3]

Abstract

Experiments are described which show that the increase in usable compression ratio obtained on adding iron or nickel carbonyl to rich mixtures with air, of hydrocarbon fuel used in the high temperature conditions of the A S T.M.-C.F.R. motor method of knock testing, is not accompanied by a commensurate increase in power The percentage by which the observed power for the doped fuel is less than that obtainable if a nonknocking fuel were used at the same compression ratio has been determined for various additions of the iron and nickel carbonyls of Fuel *S*, a commercial gasoline. The loss of possible power when using iron carbonyl in the concentration of 0 50 cc per liter, increased from 2% at maximum power mixture strength to over 22% at extremely rich mixtures The loss is attributed to appreciable oxidation of the fuel to final products, prior to the completion of compression, especially when doped fuel is used Thus the experimental results confirm the theory, advanced in Part III, that metallic antiknocks act by promoting the high temperature surface (heterogeneous) oxidation of hydrocarbon fuel to steam and carbon dioxide; not by inhibiting a homogeneous oxidation reaction by the breaking of reaction chains, as generally supposed.

Introduction

The theories that organic peroxides cause detonation and that the antiknock organometallic compounds act by destroying the peroxides or preventing their formation were first advanced by Callendar and associates (2, 3). The theories in one form or another are still current. Egerton and Gates (5) regard antiknocks "as negative catalysts which react with and remove those substances (peroxides) which auto-catalyse combustion". Egerton in a later publication (4) assumes that preflame oxidation in the engine is a homogeneous reaction, that it proceeds to ignition in the end gas by chain reactions, and that the metallic antiknocks act by breaking the chains. Ubbelohde (15, p. 2943) refers to "the complete inhibition of all oxidation by the addition of antiknocks". Prettre (12, p. 2956) concludes that "the influence of antiknocks in engines can only be explained by their inhibitory action on thermal combustion". Beatty and Edgar (1, p. 2934 and p. 2936) consider that "there is little evidence for the occurrence of significant surface reactions in an engine" and conclude that "antiknock agents act as inhibitors for the slow oxidation in the end gas. Their

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Contribution from Defence Research Board, Ottawa, Canada, in association with the Department of Mechanical Engineering, University of Toronto.
[2] *Research Scientist, Naval Division, Defence Research Board and Honorary Lecturer, Department of Mechanical Engineering, University of Toronto. Lately Director of Scientific Research and Development, Royal Canadian Navy.*
[3] *Lecturer, Mechanical Engineering, University of Toronto.*

effect is to break short the reaction chains and so prevent the chain development from reaching that critical point at which its multiplication begins".

The current theory mentioned above is no longer tenable in view of the experiments described in Parts I (6), II (7), and III (8). They show that the products of *surface oxidation* of engine fuel at *high temperatures* delay the onset of detonation or knocking combustion. The products are steam, carbon dioxide, and carbon monoxide when undoped fuels are used but when the fuel contains metallic dope the products tend to be steam and carbon dioxide only, at any temperature, and the antiknock effect is enhanced accordingly.

The difference between rates of surface oxidation of doped and undoped fuel at high temperatures and the effect of mixture strength on reaction rates were shown by experiments made when using reaction chamber No. 10 and are described in Part VII (10). Rates of reaction were found to increase by 100% on raising the temperature from 600° to 650°C. and to increase by 100% at any temperature within the range, on increasing mixture strength from 25% weak to 100% rich. Nearly 20% of the oxygen in the weak pentane–air mixture passing through the chamber was reacted at 600°C., and 80% of the oxygen in a 100% rich mixture was reacted at 650°C. Similar rates of reaction but at *temperatures 150°C. lower* were obtained when iron carbonyl was added to the pentane.

Temperatures attained by the end gas in an engine when combustion is 90% complete are estimated to be somewhat greater than 650°C. even at the low compression ratio of 4.0 (9, p. 233), and during the whole of the combustion period the "skin" surface temperatures which determine the velocity of surface oxidation would be higher to an unknown degree, because of radiation from the flame. Surface oxidation prior to completion of compression would result in a loss of power. The greater loss would occur if oxidation were promoted to final products by the use of metallic antiknocks, especially as reaction would then proceed at high velocity even at temperatures as low as 430°C. (9, p. 438).

Thus the experiments described in this Part show the *difference* in the effects on power and knock, due to surface oxidation, as between Fuel *S* and the same fuel containing iron or nickel antiknocks.

Section 1

EXPERIMENTAL ARRANGEMENTS AND RESULTS

The C.F.R. knock testing engine used for the experiments was "standard" except that arrangements were made for accurate measurement of power output.

The belt driven main and auxiliary generators of the C.F.R. unit were disconnected from the engine. The main generator was then driven as a motor from the laboratory d-c. supply and it in turn drove the auxiliary generator which supplies current for the engine auxiliaries, such as the bouncing pin, the

oil heater, the intake air heater when used, and the ignition system. The engine was then direct connected to a d-c. swinging field dynamometer with beam type scale. Thus, net brake horsepower was measured. Indicated horsepower was obtained by adding, to the B.H.P. observed when the engine was developing power, the brake horsepower required to overcome friction and pumping losses when fuel was not added to the air supply and the engine was "motored" by the dynamometer. "Motoring" loss was measured after every set of power observations as soon as possible after stopping the fuel supply.

All the experiments to be discussed were made in the conditions of the C.F.R.–A.S.T.M. motor method of knock testing; mixture temperature, 300°F.; jacket coolant temperature, 212°F.; and engine speed, 900 r.p.m.

Fuel *S*, Lot 2, a commercial grade of gasoline, generally similar to Fuel *S*, Lot 1 (11, pp. 212-213), was used for the experiments.

The experimental results are given by the graphs of Figs. 1 to 5. A uniform system of lettering is used. Thus variation of the compression ratio for standard knock intensity with increase of mixture strength is shown for the doped fuel by the A graphs and for the undoped fuel by the A_1 graphs. The variation of indicated horsepower (I.H.P.) with increase of mixture strength is shown for the doped fuel by the B graphs and for the undoped fuel by the B_1 graphs.

The term "usable C.R." will be used hereafter as an abbreviation of "compression ratio for standard knock intensity", as defined in Part VIII (9, p. 215).

It is shown by the A_1 graphs that the minimum value of the usable C.R. was obtained when the rate of fuel consumption of the undoped fuel was 1.85 lb. per hr., and, as explained in Part IX, it may be assumed that the fuel–air mixture was then approximately "correct" and consequently that percentages by which the mixture strength is rich or weak can be calculated accordingly for other rates of fuel consumption.

Nickel Carbonyl Additions to Fuel *S*

Concentration: 0.25 cc. per Liter of Nickel Carbonyl. Fig. 1

The graphs of Fig. 1 show that nickel carbonyl in the concentration in the fuel of 0.25 cc. per liter is of slight effect to increase the usable C.R. at correct mixture strength and that there is no increase of power.

Maximum power is obtained at a rate of fuel supply of 2.3 lb. per hr., that is, with a mixture strength 24% rich. The value 4.02 I.H.P. is the same for both fuels within the accuracy of measurement, although the usable C.R. for the doped fuel was 6.5 and for the undoped fuel 6.07. That is, an increase of 0.43 in usable C.R. obtained on adding the nickel carbonyl was not accompanied by any increase of power.

It will be noted that for rates of fuel consumption exceeding 2.5 lb. per hr. the large increases in usable C.R. obtained accordingly were accompanied by relatively large *decreases* in power.

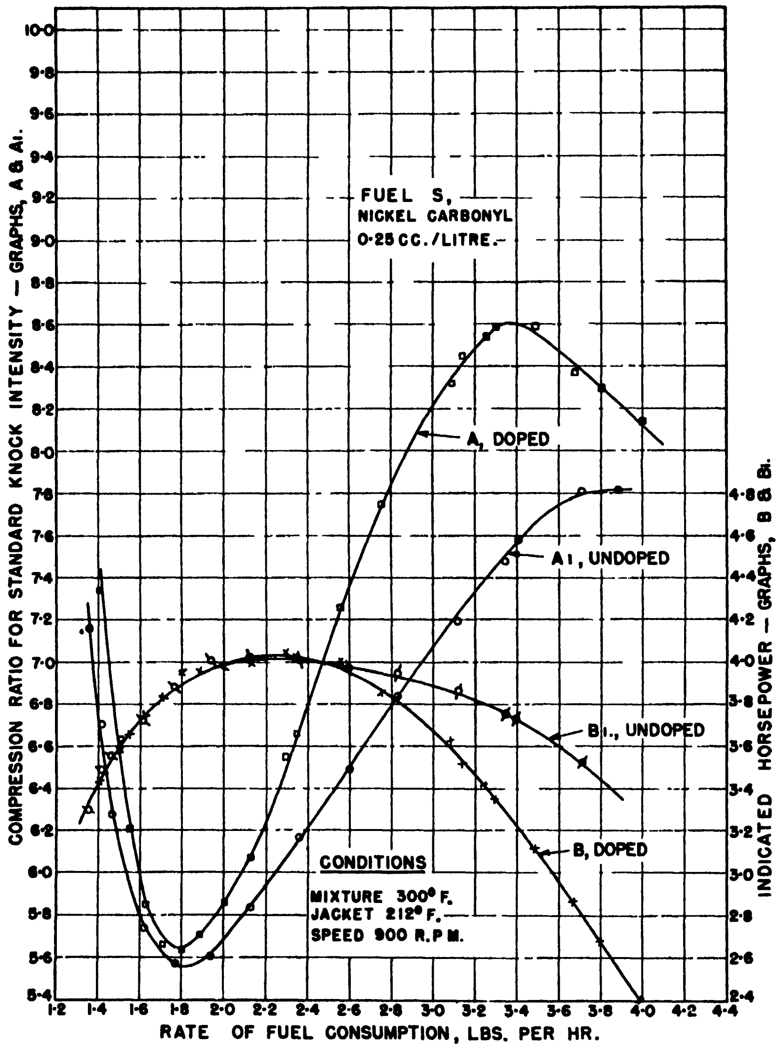

FIG. 1. *The relation between usable compression ratio and power as affected by nickel carbonyl in the fuel in the concentration of 0.25 cc. per liter.*

Concentration: 0.50 cc. per Liter of Nickel Carbonyl. Fig. 2

The effects on power and usable C.R. are shown in the graphs of Fig. 2. At the maximum power mixture strength, 2.3 lb. of fuel per hr., an increase of from 4.02 to 4.18 I.H.P. is obtained for a usable C.R. increase of from 6.07 to 6.80. The beneficial effect on power diminishes with further increase in mixture strength although usable C.R. increases rapidly, and when rate of fuel

consumption reaches 2.9. lb. per hr. the power developed by the doped mixture at a usable C.R. of 8.34 is the same as that for the undoped fuel at a usable C.R. of 6.92. The mixture strength being still further increased, usable C.R. increases accordingly but the power becomes *less* than for the undoped fuel at very much lower usable compression ratios.

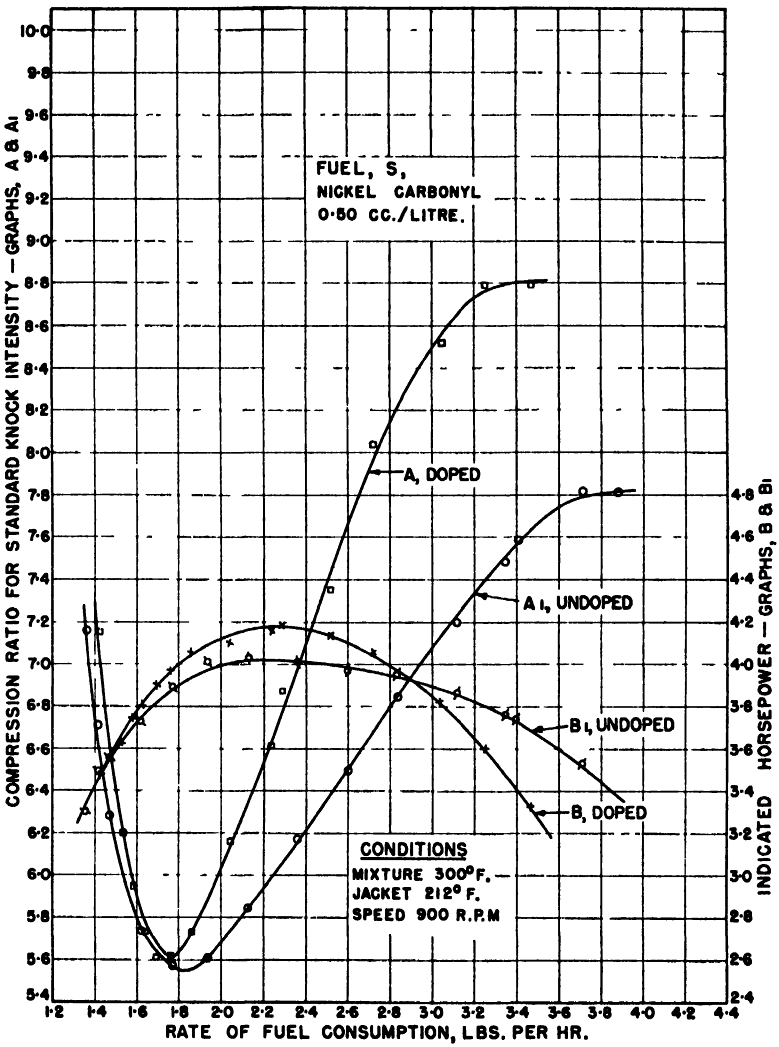

FIG. 2. *The relation between usable compression ratio and power as affected by nickel carbonyl in the fuel in the concentration of 0.50 cc. per liter.*

Concentration: 1.0 cc. per Liter of Nickel Carbonyl. Fig. 3

The effects on power and usable C.R. are shown by the Graphs of Fig. 3. At the maximum power mixture strength, 2.3 lb. of fuel per hour, I.H.P. increases from 4.02 to 4.34 for the very large increase in usable C.R. of from 6.07 to 7.85.

A usable C.R. of 10, the limiting value for the engine as used, was attained for the doped fuel on increasing the rate of fuel consumption to 2.9 lb. per hr. The increase in usable C.R. from the 6.92 of the undoped fuel was accompanied by an increase of from 3.92 to 4.15 I.H.P., that is, less than 6%.

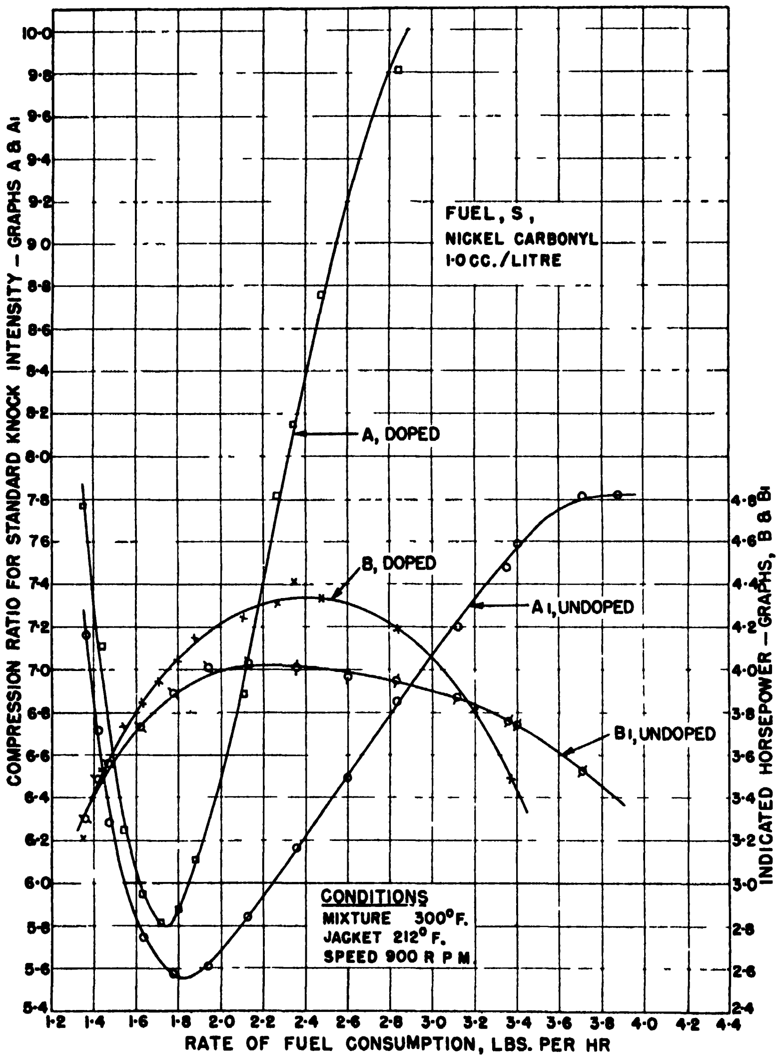

FIG. 3. *The relation between usable compression ratio and power as affected by nickel carbonyl in the fuel in the concentration of 1.0 cc. per liter.*

Equal power was developed by the doped and undoped fuels at a fuel consumption of 3.17 lb. per hr. The usable C.R. for the undoped fuel was then 7.25 but that for the doped fuel was greater than 10.

Iron Carbonyl Additions to Fuel *S*

Concentration: 0.25 cc. per Liter of Iron Carbonyl. Fig. 4

The effects on power and usable C.R. are shown by the graphs of Fig. 4. The antiknock effect of the iron in respect of weak mixtures is noteworthy. Thus the minimum value of the usable C.R. 5.68 was observed when the rate

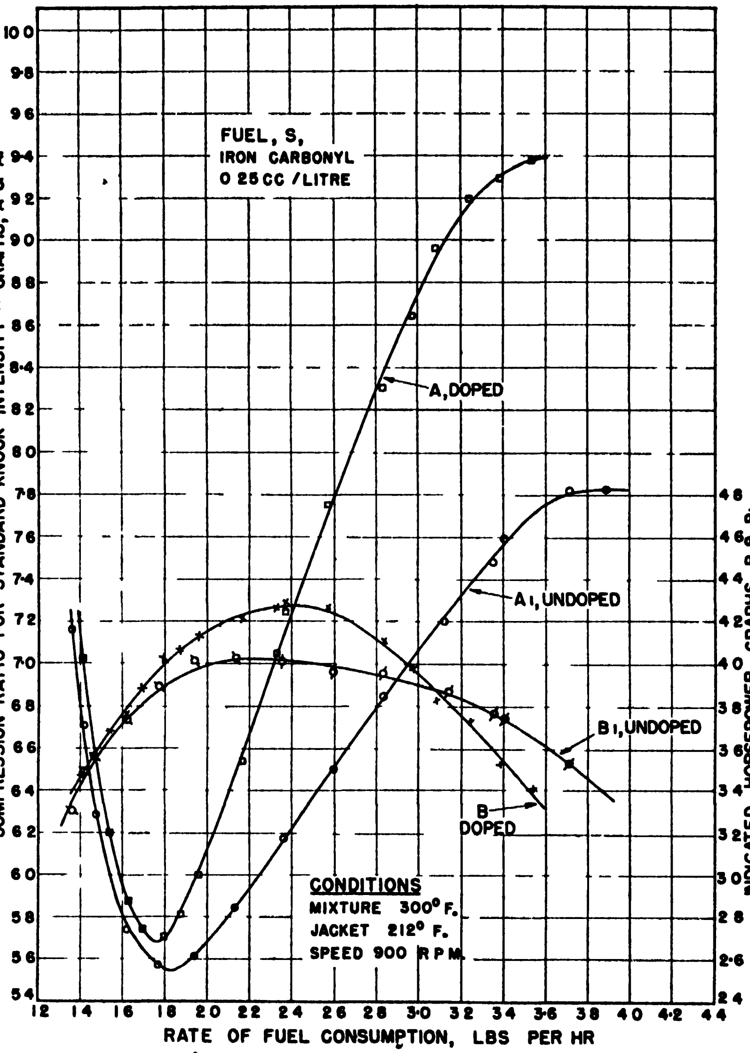

Fig 4 *The relation between usable compression ratio and power as affected by iron carbonyl in the fuel in the concentration of 0 25 cc per liter*

of doped fuel consumption was 1 76 lb. per hr , whereas when Fuel *S* was used undoped, the minimum usable C R. was 5.54, observed for a rate of fuel consumption of 1.85 lb. per hr. The I.H.P. for the undoped fuel used at 1.85 lb. per hr. was 3.93 and for the doped fuel 4.04 at the same rate of fuel consump-

tion, that is, a power increase of 2.8% was obtained on increasing the usable C.R. from 5.54 to 5.78.

The maximum I.H.P. of 4.28 was obtained for the doped fuel when the rate of fuel consumption was 2.4 lb. per hr.; the usable C.R. being then 7.28. The I.H.P. for the undoped fuel at the same rate of consumption was 4.0; the usable C.R. being then 6.21; that is, a power increase of 7% was obtained on increasing the compression ratio from 6.21 to 7.28.

The same I.H.P., namely 3.9, was obtained for both fuels when the rate of consumption was 3.1 lb. per hr. although the usable C.R. for the doped fuel was 8.95 as compared with 7.2 for the undoped fuel.

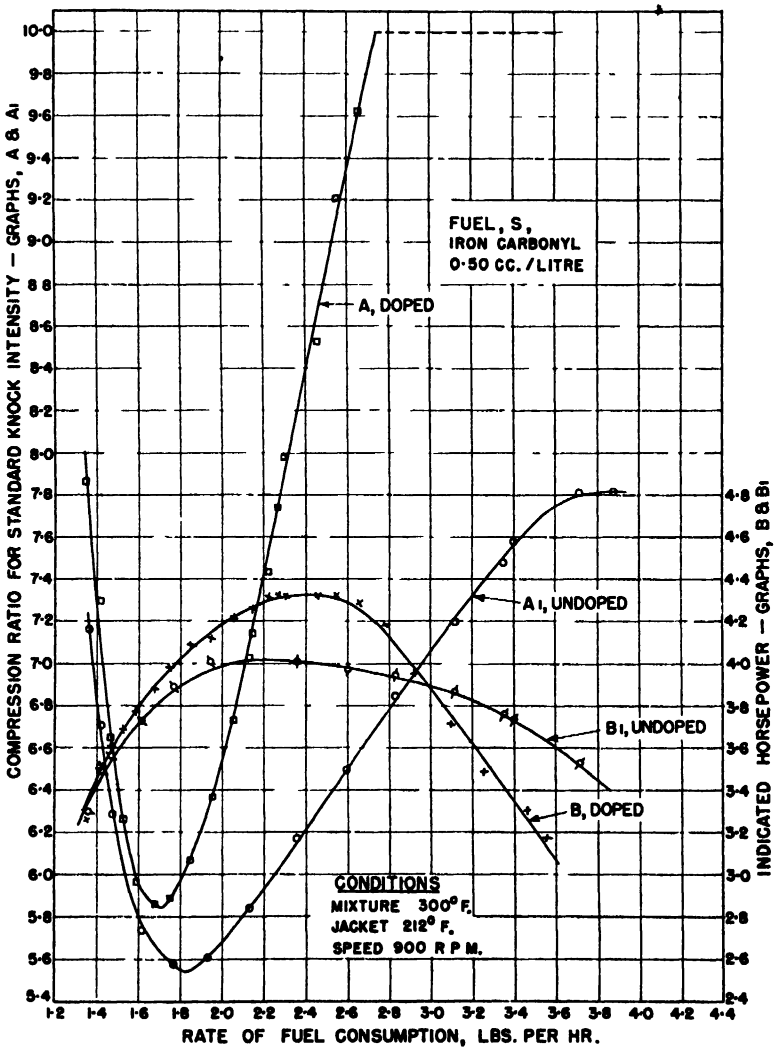

FIG. 5. *The relation between usable compression ratio and power as affected by iron carbonyl in the fuel in the concentration of 0.50 cc. per liter.*

Concentration: 0.50 cc. per Liter of Iron Carbonyl. Fig. 5

Considering a rate of fuel supply of 1.85 lb. per hr., usable C.R. increased from 5.54 to 6.07 and I.H.P. from 3.93 to 4.07, that is 3.6% on adding the carbonyl.

The maximum I.H.P. of 4.32 for the doped fuel was obtained for a rate of consumption of 2.4 lb. per hr.; the usable C.R. then being 8.4. The I.H.P. for the undoped fuel at the same rate of consumption was 4.0 and the usable compression ratio 6.21. That is, a power increase of 8% only was obtained on increasing the compression ratio from 6.21 to 8.4.

The same I.H.P., namely 3.9, was obtained for both fuels when the rate of consumption was 3.0 lb. per hr. The usable compression ratio for the undoped fuel was then 7.06, while the doped fuel was used at a compression ratio of 10, which is lower than the *usable value which could not be determined* because it exceeded the measurement limit.

Section 2

Discussion of the Experimental Results

Little if any adverse effect on power would occur if the temperature required for appreciable surface oxidation were attained late in the combustion period, which generally extends beyond top dead center. The required temperature would not, for example, be expected during compression in an unsupercharged engine at moderate compression ratios with the ingoing mixture raised in temperature solely by the usual induction pipe heating.

It has, however, been shown by laboratory experiments mentioned earlier that a fuel such as pentane doped with iron carbonyl and in rich mixtures with air is oxidized to steam and carbon dioxide with high velocity on surfaces at temperatures as low as 430°C. Higher temperatures would be expected during compression, on surfaces in the cylinders of supercharged aircraft engines, and the experimental results of Section (1) support the view that, even in the C.F.R. engine run in A.S.T.M. knock testing conditions, surface temperatures are high enough to cause preflame oxidation sufficient for an easily measurable adverse effect on power, when rich mixtures containing iron or nickel carbonyl are used.

The adverse effect on power, coincident with the antiknock effect of the metallic dopes in rich mixtures used in the C.F.R. engine, has been calculated from the experimental results of Section (1), see Tables I, II, and III below. The calculations require data for the possible percentage increase in power with increase in compression ratio for a nonknocking fuel used at compression ratios extending to 10. The data given by the graph of Fig. 6 are from those compiled by Pye (14, p. 49) for compression ratios of from 4 to 8, and have been extrapolated to a compression ratio of 10. The assumption is made that percentage increase of power with increase of compression ratio as given by the graph of Fig. 6 can be applied generally.

TABLE I

FUEL *S* PLUS 0.50 CC. IRON CARBONYL PER LITER

Rate of fuel consumption, lb /hr.	Mixture, per cent rich	Increase of usable C R.	Observed change of I H.P.	Percentage increase of I H P.	Possible % increase of I.H.P.
2 10	18.8	5 8 to 6 95	4 02 to 4 25	5 72	7 93
2 30	24 3	6 07 to 7 9	4 02 to 4 31	7 2	11 8
2 50	35 0	6 36 to 8 85	4 00 to 4 32	8 0	14 2
2 70	46 0	6 65 to 9 8	3 96 to 4 23	6 8	17 5
3 00	62 0	7 07 to +10	3 90 to 3 90	0 0	15 2+
3 40	84 0	7 57 to +10	3 73 to 3 34	−10 5	12 3+

TABLE II

FUEL *S* PLUS 0 50 CC NICKEL CARBONYL PER LITER

Rate of fuel consumption, lb /hr.	Mixture, per cent rich	Increase of usable C R.	Observed change of I H P.	Percentage increase of I H P.	Possible % increase of I H P.
2 10	18 8	5 81 to 6 27	4 02 to 4 16	3 5	3 5
2 30	24 3	6 07 to 6 81	4 02 to 4 18	3 97	4 73
2 50	35 0	6 35 to 7 37	4 00 to 4 13	3 25	6 63
2 70	46 0	6 65 to 7 90	3 96 to 4 05	2 27	7 87
3 00	62 0	7 07 to 8 50	3 90 to 3 84	−1 54	8 23
3 40	84 0	7 57 to 8 80	3 73 to 3 41	−8 6	6 15

TABLE III

FUEL *S* PLUS 1 0 CC NICKEL CARBONYL PER LITER

Rate of fuel consumption, lb /hr.	Mixture, per cent rich	Increase of usable C R	Observed change of I H P.	Percentage increase of I H.P.	Possible % increase of I H P.
2 10	18 8	5 81 to 6 9	4 02 to 4 27	6 2	6 9
2 30	24 3	6 07 to 7 86	4 02 to 4 33	7 7	11 5
2 50	35 0	6 35 to 8 8	4 00 to 4 34	9 2	14 5
2 70	46 0	6 65 to 9 55	3 96 to 4 27	7 8	16 4
3 00	62 0	7 07 to +10	3 90 to 4 05	3 9	15.2+
3 40	84.0	7 57 to +10	3 73 to 3 43	−8.0	12 3+

Thus, with reference to Table I, for example, maximum power, 4.02 I.H.P., was obtained over the range of mixture strength, 18.8 to 24.3% rich. On adding iron carbonyl in the concentration of 0.50 cc. per liter to the richer mixture, usable C.R. could be raised from 6.07 to 7.9. The corresponding increase in

I.H.P. taken from the experimental results, Fig. 5, was 7.2%. If, however, the fuel had been a nonknocking variety, the increasing of the compression ratio from 6.07 to 7.9 would have resulted in an increase of 11.8% in I.H.P. according to the data of Fig. 6. That is, attainment of the higher usable compression ratio by the use of metallic antiknock was accompanied by a loss of 4.6% of the possible increase in I.H.P.

The power obtainable when using rich mixtures of *undoped* fuel may be affected adversely by the enhanced tendency of such mixtures to oxidize on surfaces in the combustion space of the C.F.R. engine when operated in the high temperature conditions of the A.S.T.M. knock testing method. There-

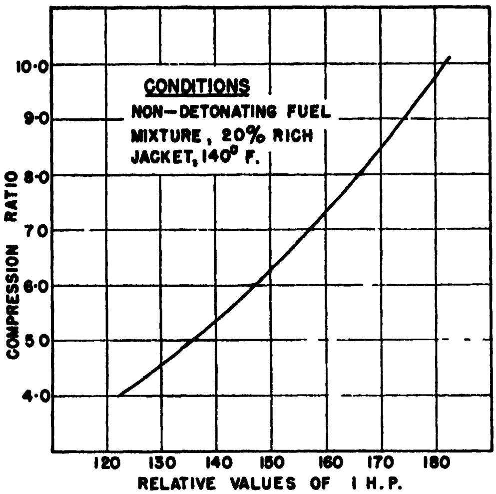

FIG. 6. *The relation between compression ratio and power for a nonknocking fuel used in the Ricardo E 35 engine.*

fore, the experimental results given in this paper are regarded as representing differences in the adverse effect on power of surface oxidation, between Fuel *S* and the same fuel containing iron or nickel antiknock.

Mixture strengths given in the tables range from 18.8 to 84% rich. The maximum I.H.P., Fuel *S*, was constant within the accuracy of measurement over the mixture range 19 to 35% rich and at 84% rich it was 6% only, less than at 2.8% rich. When an engine is run with the compression ratio fixed, it is usually found that power reaches a maximum within the mixture range 10 to 20% rich and diminishes slowly with further increase (13, p. 134). It is to be noted accordingly that values of I.H.P. given in the tables were obtained on increasing compression ratio with increase of mixture strength to maintain a standard knock intensity.

The loss of possible I.H.P. coincident with the antiknock action of the iron and nickel carbonyls is shown by differences between the percentages of Columns 5 and 6 of the tables.

It will be noted by reference to Tables I and II that iron carbonyl in the concentration of 0.50 cc. per liter possesses nearly the same antiknock effect as nickel carbonyl in double the concentration. It will suffice, therefore, to mention the principal features of the experimental results obtained when using iron carbonyl.

The possible loss of power coincident with the antiknock action of iron carbonyl in the concentration of 0.50 cc. per liter, Table I, extends from 2 to nearly 11% as mixture strength is increased from 19% to 46% rich. The loss at 62% rich was greater than 15% and at 84% rich it was greater than 22%. The full extent of the losses at mixture strength greater than 46% rich could not be measured because the compression ratio was then off the scale of the engine when the doped fuel was used.

Concluding Comment

The principal interest of the experimental results lies in their confirmation of the theory, advanced in Part III (8), that the metallic antiknocks act by *promoting* the high temperature surface oxidation of hydrocarbon fuel to steam and carbon dioxide, not by inhibiting a homogeneous oxidation reaction by breaking reaction chains.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and Assistant Prof. W. A. Wallace. Dynamometer equipment was generously lent by the National Research Council, Montreal Road Laboratory. The cost was defrayed in part by an Extramural Grant from the Defence Research Board (Canada).

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THE PREPARATION OF QUINOLINES BY A MODIFIED SKRAUP REACTION[1]

By Richard H. F. Manske,[2] Archie E. Ledingham,[3] and Walter R. Ashford[3]

Abstract

It has been found that a modification in the method of bringing together the reactants of Skraup's procedure for synthesizing quinolines results in a marked reduction of the violence of the original reaction and in a substantial increase in yield of quinoline or substituted quinoline. The ease of carrying out the reaction is such that it can be utilized safely and economically on a commercial scale. Examples of the modified method are given for quinoline, 8-hydroxyquinoline, and 5-chloro-8-hydroxyquinoline. The method was applied to the Doebner–von Miller reaction for the synthesis of 8-hydroxyquinaldine and 5-chloro-8-hydroxyquinaldine with somewhat less improvement than in its application to the Skraup reaction.

Discussion

Since the date of its discovery, 1880, the Skraup reaction has been the subject of many researches, the objects of which were to decrease the violence of the reaction and to increase the yields. As originally carried out by Skraup (13) for the preparation of quinoline, the reaction consisted in heating together one part by weight of aniline with one and one-half parts by weight of sulphuric acid and one or more parts of glycerol to 180° to 190°C. The reaction was exceedingly violent in the initial stages and produced a small yield of quinoline. The addition of nitrobenzene to the mixture (14) raised the yield of quinoline to about 50% based on the aniline used.

Subsequent modifications in the process have replaced the nitrobenzene by inorganic oxidizing agents such as arsenic acid (9), picric acid (8), and calcined ferric oxide (1). Recently, the nitrobenzene has been replaced by a small quantity of iodine (7), while the violence of the reaction has been moderated by the use of such reagents as acetic acid (3) and boric acid (4), both of which are believed to form a compound with the glycerol, thereby controlling the amount of free glycerol present in the reaction mixture. Acetylation of the amine (10) has been shown to improve the yield and the ease of operation of the Skraup process.

Modifications in the mode of bringing the reactants together such as adding the sulphuric acid portionwise (5, 11) have not resulted in eliminating the danger of violent reaction and in producing high yields.

It has been observed that the mode of reacting the original Skraup chemicals for the quinoline synthesis is all-important in the matter of control of the vigor

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Contribution from the Research Laboratories, Dominion Rubber Company Limited, Guelph, Ontario.
[2] *Research Director.*
[3] *Research Chemist.*

of the reaction and in the attainment of high yields. The Skraup reactants, namely, glycerol, amine, nitro compound, and sulphuric acid can be mixed with temperature control and then maintained at any convenient temperature up to 120° C. without appreciable chemical reaction taking place. This premix, maintained at a temperature that keeps it fluid (60° to 90°C.), is added in portions to a reaction vessel where each is warmed with stirring to 140° to 170°C. at which temperature the Skraup reaction begins to take place. When the entire mixture has been transferred in this manner, it is heated and stirred under reflux for four to six hours, the end of the reaction being indicated by the disappearance of nitro compound from the reflux liquors. During this time the temperature of the mixture under reflux drops to about 127° to 130°C., owing primarily to the formation of water.

With this procedure, there is no tendency for a violent reaction—in fact heat must be applied continually to maintain the temperature of reaction (135° to 140°C.). It is noteworthy, also, that reaction proceeds at a lower temperature than when other modifications are employed, providing for a smoother reaction and the attainment of higher yields–up to 40% increase. In addition it has been possible to use just sufficient nitro compound so that all of it is consumed in the reaction and there is no need for the recovery of an unused portion.

The principal variables in the reaction have been studied and their most effective adjustment can be described as follows.

1. *Amounts of Reactants*

The effect of variation in the amounts of glycerol and nitro compound employed in relation to the quantity of amine used was studied. In the case of quinoline, it was found that a ratio of from 2 to 2.6 moles of glycerol to one of aniline served to give maximum yields. Lower glycerol–aniline ratios caused a decrease in yield.

For the synthesis of 8-hydroxyquinoline, maximum yields were obtained using a ratio of 3.1 moles of glycerol to 1 mole of *o*-aminophenol. Good yields were maintained with a ratio of 2.7 to 1, but with lower ratios, the yield dropped off. (Table I, Expts. 1 to 8.)

Nitrobenzene or other aromatic nitro compound is used in such quantity as to provide sufficient oxidizing power when the nitro body is completely or almost completely consumed in the reaction. In the case of quinoline, a ratio of 0.535 mole of nitrobenzene to 1 of aniline produced the best yields. Decreasing the ratio to 0.38 to 1 caused a large drop in yield, while increasing it to 0.72 to 1 necessitated the recovery of considerable nitrobenzene. In the case of 8-hydroxyquinoline, a ratio of 0.5 mole of nitro body to 1 mole of amine was found to be the most desirable (Table I, Expts. 9 to 13). However, in the case of 5-chloro-8-hydroxyquinoline somewhat less than the 0.5 to 1 ratio for nitro compound was found to give excellent yields (Expt. 13, Table I).

The use of relatively small quantities of ferrous sulphate ($FeSO_4.7H_2O$) gave noticeable improvements in the yields of quinoline as indicated in Expts. 14 to 16, Table I, and had a beneficial effect upon the smoothness of the reaction.

TABLE I

OPTIMUM QUANTITIES OF REACTANTS FOR MODIFIED SKRAUP REACTION

Expt.	Amine (A), gm.	Glycerol (B), gm.	Molar ratio (A) to (B)	Nitro compound (C), gm.	Molar ratio (A) to (C)	H_2SO_4, gm.	Yield		Remarks
							Gm.	%	
1	Aniline 106	200	1 : 1 9	75	1 : 0.54	364	137	93 1	% yield based on amine
2	Aniline 106	220	1 : 2 1	75	1 : 0 54	364	146	99 1	" " " " "
3	Aniline 106	271	1 : 2 58	75	1 : 0 54	364	146	99 1	" " " " "
4	o-Amino phenol 56 3	98	1 : 2 1	36 3	1 : 0 5	157	64	85 7	" " " " "
5	o-Amino phenol 28 2	63	1 : 2.7	18.2	1 : 0.5	79.1	36	96.5	" " " " "
6	o-Amino phenol 112 6	252	1 : 2 7	72.6	1 : 0.5	314	143 2	96	" " " " "
7	o-Amino phenol 112	286 8	1 : 3.1	72 6	1 : 0 5	314	154.4	103	" " " " "
8	o-Amino phenol 28 2	80 5	1 : 3 4	18 2	1 : 0 5	79 1	36	96 5	" " " " "

TABLE I—*Continued*

Expt.	Amine (*A*), gm.	Glycerol (*B*), gm.	Molar ratio (*A*) to (*B*)	Nitro compound (*C*), gm.	Molar ratio (*A*) to (*C*)	H_2SO_4, gm.	Yield		Remarks
							Gm.	%	
9	Aniline 106	271	1 : 2 58	50	1 : 0 36	364	112	76.2	Expts. 9 to 13 show effect of variation of quantity of nitrobenzene
10	Aniline 106	271	1 : 2 58	75	1 : 0 54	364	146	99 1	
11	Aniline 106	271	1 : 2 58	82	1 : 0 59	364	148	100 5	
12	Aniline 106	271	1 : 2 58	100	1 : 0 72	364	145	98 5	18 gm. nitrobenzene recovered
13	4-chloro *o*-amino phenol sulphate 192 6	290	1 : 3 2	86 8	1 : 0 5	260	196	109	7 gm. nitro compound recovered
14	Aniline 106	271	1 : 2 58	75	1 : 0.54	364	104	70.6	$FeSO_4$ omitted
15	Aniline 106	220	1 : 2 1	75	1 : 0.54	364	146	99.1	10 gm. $FeSO_4$ added
16	Aniline 106	271	1 : 2 58	75	1 : 0 54	364	148	100 5	20 gm. $FeSO_4$ added

2. *Combination of Reactants to Form the Premix*

The following is the preferred order for combining the reactants. The amine and the glycerol were added to the concentrated sulphuric acid in that order, with cooling, so that the temperature was maintained at 70° to 90°C., the mixture being kept fluid and transferable. The other two reactants, the nitro body and ferrous sulphate, were placed in the reaction vessel ready to be treated, in portions, with the premix.

3. *Temperatures*

The temperature of the glycerol–sulphuric acid–amine mixture in the case of all the quinolines studied could be raised to 120°C. without reaction proceeding. In the case of quinoline, the temperature during the portionwise addition of the premix was allowed to rise to 160° to 172°C., while during reflux the temperature varied from 150°C. at the beginning to about 135°C. at the end of the reaction. With substituted quinolines, the temperature rarely exceeded 145°C. during the addition of the premix, while during the reflux period the temperature gradually dropped to 129° to 131°C.

4. *Rate of Addition of Premix*

The glycerol–sulphuric acid–amine premix was added to the reaction vessel at such a rate that the vigor of the reaction produced by each portion had subsided before the next portion was added. However, the procedure described in the paper allows considerable leeway and there is no danger of the violence of the usual Skraup reaction.

5. *Stirring*

It is preferable to stir the mixture in order to get equal distribution of heat of reaction. However, stirring is not absolutely essential.

6. *Time of Reaction*

The reaction was complete in four to five hours of heating and stirring following the addition of the last portion of the premix. The end of the reaction was indicated by the disappearance of nitro compound from the reflux liquors

7. *Separation of the Product*

In the preparation of quinoline, the base was recovered from the reaction mixture in a good state of purity by a steam distillation. Pure quinoline was obtained by a single distillation. In the case of 8-hydroxyquinoline, the product was isolated from the Skraup reaction mixture, following neutralization, by (1) steam distillation, (2) filtering oft the precipitate, drying, and separating the product by vacuum distillation, or (3) precipitating it as the copper (or other metal) salt with control of the pH.

With substituted quinolines, for example 8-hydroxyquinoline, the difficulty is to separate the base from undesirable tarry by-products in a cheap, convenient way. To accomplish this, the neutralized Skraup mixture, which contained the precipitated quinoline and tarry by-products, was treated with suffi-

cient sulphuric acid to dissolve the base and leave the tarry material largely undissolved. The mixture was then stirred at 95° to 100°C. for one-half hour, which treatment served to coagulate the tarry material and facilitate its removal by filtration when the mixture had cooled. This treatment was repeated if necessary, but one such procedure usually served to remove 90% of the undesired material. The acid filtrate was then treated for removal of the 8-hydroxyquinoline as the copper salt.

The pH of the solution has an important effect upon the precipitation of 8-hydroxyquinoline as the copper salt. According to Prodinger (12) copper 8-quinolate is not precipitated below pH 2.2, precipitation is incomplete at pH 2.2. to 2.7, and complete within the range 2.7 to 14. The copper complex precipitates over a wider range than that of any other metal.

The filter cake of copper 8-quinolate normally will contain considerable water which is difficult to remove even on long suction under vacuum. It has been found best to allow most of this water to escape at a fairly low temperature in a current of air rather than try to remove it rapidly at a higher temperature. Thus the filter cake was dried at around 50°C. in a current of air to remove the excess moisture, then pulverized and dried for two hours at 110°C. to remove water of crystallization. The copper salt of 8-hydroxyquinoline is stable to heat at 100°C. for long periods and to sunlight during long exposure.

Experimental

Quinoline

Freshly distilled aniline (106 gm.) and glycerol (220 gm. U.S.P.) were added, in that order, to concentrated sulphuric acid (364 gm.) in a three-liter, three-necked, round-bottomed flask with cooling, so that the temperature was within the range 70° to 90°C. The mixture was then maintained in a fluid state until ready for use by placing it on a steam bath.

The reaction vessel consisted of a three-liter, three-necked, round-bottomed flask fitted with a stirrer, thermometer, and reflux condenser. The flask was charged with a mixture of freshly distilled nitrobenzene (75 gm.) and ferrous sulphate ($FeSO_4.7H_2O$, 10 gm.), which was heated to 100° to 120°C. with stirring in preparation for receiving the premix of acid, aniline, and glycerol described above.

The premix was then added in about 10 portions to the reaction vessel, reaction being allowed to proceed at 160° to 170°C. before each subsequent portion was added. When all the premix had been transferred to the reaction vessel, the mixture was stirred and refluxed for four hours during which time the temperature gradually dropped to 135° to 140°C.

At the end of the reflux period, the acid mixture was steam distilled to remove any unused nitrobenzene, made alkaline with 50% sodium hydroxide solution, and steam distilled, the heat of neutralization being sufficient to initiate the distillation. The crude product was separated from the aqueous mixture and vacuum distilled, b.p. 109°C. (14 mm.). $n_D^{25} = 1.6232$.

The quinoline produced by this method has a purity of 98 to 99% and contains 0.2 to 0.8% aniline, 0.2 to 0.8% nitrobenzene and a trace of moisture.

8-Hydroxyquinoline

A premix of reactants was made by treating concentrated sulphuric acid (169 cc. 96%) with *o*-aminophenol (112.6 gm.) and glycerol (286.8 gm. U.S.P.) in that order, with cooling and stirring so that the temperature did not exceed 80°C.

o-Nitrophenol (72.6 gm.) and ferrous sulphate ($FeSO_4.7H_2O$, 10 gm.) were added to the reaction vessel as in the case of quinoline and heated to 100° to 120°C. in readiness to receive portions of the premix.

The amine–glycerol–acid premix was added to the reaction vessel in about 10 portions over two hours, reaction being allowed to proceed at 135° to 150°C. before each subsequent portion was added. The reaction mixture was refluxed for another four hours, during which time the temperature dropped to 129° to 131°C.

(*a*) *Separation of Product by Distillation.*—The cooled reaction mixture was neutralized with sodium hydroxide (250 gm. in 50% solution) with rapid stirring and addition of pieces of ice so that the temperature did not exceed 40°C. This quantity of alkali was sufficient to bring the solution to pH of about 7 and to cause the precipitation of the hydroxyquinoline, tarry by-products, and some inorganic matter. The entire precipitate was filtered off, air-dried at 50° to 60°C., introduced into a distilling flask with a short Vigreux column, warmed under vacuum to melt the 8-hydroxyquinoline (m.p. 76°C.) and then distilled *in vacuo*. Residual water was first removed and then the 8-hydroxyquinoline collected at 95° to 105°C. (3 mm.) (100° to 110°C. (5 mm.)). The product from such a run weighed 143.2 gm. (the theoretical yield based on amine used is 149.8 gm.) and consisted of a white solid melting at 74° to 75°C.* The hydrochloride, consisting of yellow needles, melted at 234° to 235°C. after recrystallization from methanol–ether. Calc. for $C_9H_7NO.HCl$; C, 59.5; H, 4.44. Found: C, 59.64; H, 4.48.

(*b*) *Separation of Product as the Copper Salt.* The reaction mixture was neutralized as before. This caused the precipitation of the free quinoline plus a quantity of undesirable tarry by-products. Sufficient concentrated sulphuric acid in 25% solution (42 cc. concentrated sulphuric acid) was added to the mixture to dissolve the hydroxyquinoline. This left the tarry material largely undissolved. The mixture was stirred at 95° to 100°C. for 0.5 hr., which treatment served to coagulate the tarry material and facilitated its removal by filtration from the cooled mixture. The amber-colored filtrate had a pH of 1.5 to 2.5 and was treated with copper sulphate (130 gm. $CuSO_4.5H_2O$) in 25% solution. This caused a further lowering of the pH. The addition of sodium hydroxide (90 gm.) in 50% solution precipitated the copper salt quantitatively

* *Melting points are corrected.*

from the mixture as a bright green water-insoluble material. It was filtered immediately from the warm solution and washed thoroughly with water to remove inorganic material. The yield of material dried at 110°C. for two hours, after a preliminary drying at 50°C. in a current of air and grinding to a powder, was 190 gm. of 90 to 95% purity. The copper present in the copper 8-quinolate was determined gravimetrically by the method of Berg (2), which consisted of igniting a sample of the copper salt cautiously to cupric oxide in the presence of oxalic acid.

5-Chloro-8-hydroxyquinoline

The method employed for this substituted quinoline was similar to that described for 8-hydroxyquinoline above. The 4-chloro-*o*-aminophenol used was obtained by the reduction of 4-chloro-2-nitrophenol over Raney nickel in methanol, which reduction proceeded quantitatively at 50 lb. pressure of hydrogen and a temperature of 60° in two to three hours. The 4-chloro-*o*-aminophenol was isolated from the methanolic solution as the sulphate salt after filtering off the nickel catalyst, treating with the required quantity of sulphuric acid in methanol, and concentrating to dryness.

The modified Skraup was carried out as described above using 4-chloro-*o*-aminophenol sulphate (192.5 gm., 1 mole) concentrated sulphuric acid (139 cc., 96%), glycerol (290 gm., U.S.P.), 4-chloro-2-nitrophenol (86.75 gm., 0.5 mole) and ferrous sulphate ($FeSO_4.7H_2O$, 10 gm.). The heating period, following addition of the premix to the reaction flask, was 6.5 hr., the initial temperature being 140° to 150°C. and the final temperature of reflux, 127°C. The completed reaction mixture was steam distilled to remove 7 gm. of unreacted 4-chloro-2-nitrophenol (Table I, Expt. No. 13).

The steam distillation residue was neutralized with 50% sodium hydroxide solution and then made faintly alkaline with sodium carbonate, whereupon the substituted quinoline separated as the free base. The filtered, dried product weighing 248 gm. was dissolved in 5 liters of alcohol and the solution filtered to remove some insoluble black material. The total quantity of by-product tarry material from the reaction was 73 gm. The alcoholic solution was treated with charcoal, boiled, filtered, and concentrated to cause separation of the product as a yellowish-brown crystalline material, weight 196 gm. Yield, 109% based on 4-chloro-2-nitrophenol used for corresponding amine, m.p. 127.5° to 128.5°C. Previously reported values, 130°C. (15), 122° to 123°C. (6). The picrate, consisting of fine yellow needles, recrystallized from methanol melted at 214° to 215°C. Calc. for $C_9H_6ON.Cl.\ C_6H_3O_7N_3$; C, 44.06; H, 2.2. Found: C, 44.21; H, 2.26.

8-Hydroxyquinaldine

The modified procedure for Skraup's quinoline synthesis, the subject of this paper, was applied to the preparation of 8-hydroxyquinaldine but the yields obtained were no better than when the usual method involving crotonaldehyde was employed. The method follows.

o-Aminophenol (110 gm., 1 mole) was added slowly to dilute sulphuric acid (500 cc., 32%), dissolved, and cooled. Crotonaldehyde (105 gm., 1.5 moles) was then added to the mixture with cooling, so that the temperature did not exceed 30°C. This mixture was run into a flask containing *o*-nitrophenol (70 gm.) over a period of three hours with the temperature at 95° to 100°C. The entire reaction mixture was then stirred for an hour longer at 105°C. Steam distillation of the acid reaction mixture gave 40.5 gm. of unchanged *o*-nitrophenol and caused the separation of about 75 gm. of tarry material from the steam residue. The acid liquor was filtered, made neutral with sodium hydroxide, and then slightly alkaline with sodium carbonate, whereupon the product separated as an orange-brown solid. It was taken up in chloroform, dried, filtered, concentrated, and distilled *in vacuo*. Almost the entire mass of residue came over at 105° to 110°C. (3 mm.) as a colorless to yellow oil. Yield, 111.3 gm. or 70% based upon amine used. On cooling, the product consisted of yellow needles and after recrystallization from methanol melted at 228° to 229°C. (decomp.). Calc. for $C_{10}H_9NO.C_6H_3O_7N_3$: N, 14.43%. Found: N, 14.42%.

5-Chloro-8-hydroxyquinaldine

The above method was applied to the preparation of 5-chloro-8-hydroxyquinaldine but low yields were obtained. The following reactants were used: 4-chloro-*o*-aminophenol sulphate (77 gm., 0.4 mole), 4-chloro-2-nitrophenol (34.7 gm., 0.2 mole), dilute sulphuric acid (188 cc., 30%), and crotonaldehyde (42 gm., 0.6 mole). The mixture was heated at 90° for 1.5 hr. following addition of reactants and then for a further 1.75 hr. at 100° to 105°C. On steam distillation 24 gm. of 4-chloro-*o*-nitrophenol was obtained. Separation as described above followed by distillation yielded 20 gm. of product boiling at 110° to 120°C. (3 mm.). Theoretical yield based on amine is 77.4 gm. Yield, 25.8%, m.p. 69° to 71°C. The picrate, from methanol, dried at 100°C. for two hours melted at 211° to 212°C. Calc. for $C_{10}H_8NOCl.C_6H_3O_7N_3$; N, 13.25% Found: N, 13.31%.

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POLAROGRAPHIC DETERMINATION OF THE GAMMA ISOMER OF BENZENEHEXACHLORIDE IN INSECTICIDES AND SOIL[1]

By H. Grass[2] and E. Y. Spencer[3]

Abstract

A precise and simple method for the determination of the gamma isomer of benzenehexachloride in commercial insecticides and soil by the dropping mercury electrode is outlined. A satisfactory supporting electrolyte consisted of 1% potassium iodide and a trace of gelatin in 50% ethanol.

Introduction

The discovery of the activity of the gamma isomer of benzenehexachloride as an effective insecticide has intensified the need for the development of a simple, rapid, and precise method for its determination. Biological, infrared (2), cryoscopic (1), and partition chromatographic (1) methods have been utilized but are either very time-consuming or require expensive equipment. In recent polarographic studies it was found that only the gamma isomer was reducible at the dropping mercury electrode, and determinations based on this observation have been described (3, 4). The method to be outlined here is less complicated and more satisfactory than the one described by Dragt (3). The modified procedure gave accurate results for estimation of the gamma isomer in synthetic mixtures and in commercial preparations with a variety of carriers and diluents and it also provided a means of estimating recovery from the soil.

Method and Materials

The liquid medium found most suitable to dissolve the benzenehexachloride, the maxima eliminator, and the supporting electrolyte was a 50% solution of ethanol. Methyl red, starch, and gelatin were investigated as maxima suppressors, and, of these, gelatin even in concentrations as low as 0.005% proved the best.

Three indifferent electrolytes were examined; potassium chloride, bromide, and iodide. The first two were not satisfactory, whereas potassium iodide in a concentration of 1% was found to be suitable. Thus the supporting electrolyte consisted of a 50% ethanol solution containing 1% potassium iodide and a few grains of gelatin.

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.
[2] *Fourth Year Chemical Engineer.*
[3] *Associate Professor.*

The diffusion current was proportional to the gamma isomer in the concentration range 10^{-3} to 10^{-5} molar. Below this concentration the accuracy was low, while above it the values started to deviate from linearity. The range found most satisfactory for quantitative determination was between 0.005 and 0.004%.

A cell was constructed that consisted of two compartments, one a calomel electrode connected to the other by means of a salt bridge composed of a fused glass plug and an agar gel saturated with potassium chloride. The other half of the cell contained the test solution into which dipped the capillary. Another capillary was sealed to the bottom of this cell through which hydrogen or nitrogen was passed and through which the test solution was drawn at the end of a determination. The temperature of the cell was maintained at 25 ± 0.25°C. in a water bath. A mercury head of 45 cm. was used while the readings were made with a Sargent model XII instrument.

A sample of suitable size to give a concentration of the gamma isomer within the desired range was dissolved or suspended in the supporting electrolyte. An aliquot of the solution or supernatant liquid was added to the cell, and nitrogen or hydrogen was bubbled through for 20 min. The flow of gas was then stopped and the mercury allowed to start dropping, to prevent plugging of the tip during immersion. The capillary was then lowered into the solution. (A rubber dam surrounding it covered the mouth of the cell and thus excluded oxygen.) This was followed by raising the mercury reservoir to the 45 cm. mark.

Two volts, as read on the voltmeter, was then applied to the system and the current was measured over the range −0.4 to −1.9 v. The current was plotted as an average of the galvanometer oscillations, the wave height measured, and the concentration determined from the calibration curve. The calibration was carried out with known concentrations of the pure gamma isomer by plotting the wave heights against the gamma isomer concentration. Since impurities in the various compounds tested increased the residual current by varying amounts, the whole curve had to be plotted for each sample and the wave height determined by the tangent-intercept method.

The samples assayed that contained the gamma isomer included crude benzenehexachloride containing all the isomers, synthetic mixtures, and commercial preparations with a talc base or added mercury compounds.

The soil samples were extracted with three successive portions of ether, the solvent was evaporated, and the residue dispersed or dissolved in a suitable amount of the supporting electrolyte.

Results and Discussion

The half-wave potential was found to be −1.35 v. and the wave appeared between −0.8 and −1.8 v., all versus the saturated calomel electrode. The dropping mercury electrode possessed an m value of 1.39 mgm. per sec. The

drop time was 3.9 sec. at −1.8 v. and 3.8 sec. at −1.0 v. with 0.025% gamma isomer in the electrolyte employed.

Results obtained, using a sensitivity of 50 over a concentration range of 0.04 to 0.01 gm. per 100 ml., are shown in Table I.

TABLE I

WAVE HEIGHT VARIATION WITH GAMMA ISOMER CONCENTRATION

Concentration gamma isomer, %	Wave height in divisions of galvanometer deflection			
	Solution 1		Solution 2	
0 040	52	50	51	50
0 035	45	44	44 5	44 5
0.030	37 5	38	39	38
0.025	31 5	30	31	31
0 020	25	24 5	26	25
0 015	20	19	20	19.5
0.010	11	12	13	12

It was found that the other isomers in the crude material, talc, or mercury compounds that are added to some commercial products had no effect on the wave height for the gamma isomer. In the concentration range 10^{-3} to 10^{-4} molar an accuracy of approximately ± 0.5% was obtained. This required averaging several polarographs in order to reduce inaccuracy in plotting, measuring, and averaging galvanometer deflections. A commercial talc base preparation stated to contain 25% of the gamma isomer assayed 24.0% by the above method.

A soil sample that was taken from a plot that had been treated the previous season with gamma isomer at a concentration of 10 lb. per acre and a control sample yielded ether extracts that gave no indication of the presence of any gamma isomer. On the other hand a 25% recovery of the gamma isomer was obtained from a soil sample to which gamma isomer had just been added at the same concentration as to the field sample.

The absence of any gamma isomer in the field sample is not surprising since benzenehexachloride is known to be hydrolyzed, particularly in an alkaline medium and in soils. Recovery of only one-quarter of the recently added isomer is probably due to its partial adsorption. Greater recovery might be obtained by prolonged extration. However, of significance was the fact that considerable of the gamma isomer could be recovered in the ether extract and determined with no interference from the other ether-soluble material.

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THE EFFECT OF ADDED WATER AND ANTIOXIDANTS ON THE KEEPING QUALITY OF LARD[1]

BY H. J. LIPS[2]

Abstract

Moisture alone had little detrimental effect on lard storage life (time at 90° F. to attain a peroxide oxygen value of 10 ml of 0.002 *N* thiosulphate per gm.) except at the highest levels of incorporation (up to 12.8%), but citric acid, lecithin, and alpha-tocopherol had more stabilizing action in dry lard than in lard containing water. Gum guaiac gave the greatest increase in storage life and citric acid the least. The stabilization varied with the original quality of the lards tested (two wet rendered, two dry rendered, and two composite lards) but no segregation of the results according to wet and dry *rendering* of these lards was possible.

Introduction

The presence of water in fat tends to increase enzymic and microbial changes and may affect oxidative deterioration. In the few investigations of the direct action of water on fat oxidation various results have been reported. With butterfat a small (unstated) concentration of added water had no effect (3), 4% water extended the induction period (9), and 16% water accelerated oxidation in one study (11) but had no effect in another (19). The addition of small amounts of water to dried lard did not change its stability (6). The induction period of vegetable oils was reduced by treatment with boiling water, presumably because natural antioxidants were destroyed (18). In systems containing constituents other than fat, water may act indirectly as an antioxidant by increasing the stabilizing action of water-soluble substances, or by stimulating microbial growth which may produce a condition unfavorable for oxidation of the fat (12, p. 184). In the wet rendering of lard, it is important to exclude tankage water, which carries food for bacteria. Water may destroy the activity of stabilizers for dry fats (12, p. 174), or increase the activity of certain antioxidants (15). Because of the limited information available it was considered of interest to study the effect of moisture on fat oxidation, using as experimental materials Canadian lard and the antioxidants permitted for use in Canada.

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[2]*Biochemist, Oils and Fats Laboratory.*

Materials and Methods

To investigate the effect of water on the stability of representative lards produced in Canada, 75-lb. batches of two wet rendered lards (*A* and *B*) and two dry rendered lards (*C* and *D*), free of added antioxidants, were obtained from four plants. These were selected on the basis of a previous survey (14) to secure both poor (*A* and *C*) and fair (*B* and *D*) samples of each of the two types. Two mixtures (*E* and *F*), each containing several wet and dry rendered lards, were also used as test materials.

Preparation of Storage Samples

Preliminary experiments indicated that all the water in 3000 to 3500 gm. lots of commercial lard (about 0.1% moisture) could be removed by heating under vacuum in a boiling water bath, with continuous agitation, for three hours. The lard was considered dry if a 2 gm. sample remained constant in weight when heated in a vacuum oven for two hours at 122° F. (1).

Preliminary work also demonstrated that an emulsion of water in lard containing up to 12% water was stable when chilled and then brought to room temperature, but above this moisture level there was some separation of water. Incorporating water by beating or stirring solid or liquid lard was a lengthy procedure and it was difficult to obtain a uniform mix. Two types of colloid mills were unsuitable for this purpose because the lard was heated too drastically during the milling process. Finally, a Waring Blendor was found to produce a reasonably stable emulsion without excessive temperature rise, when components initially at room temperature were blended for five minutes and then cooled immediately at 25° F. Cooling at lower temperatures caused separation of some of the added water.

The following procedure for preparation of samples was adopted. Melted, dry lard (500 gm.) was weighed into Waring Blendor jars and measured amounts of redistilled water added. The lard was allowed to become semisolid at room temperature before blending to minimize loss of water by evaporation and to produce a tighter emulsion. The Blendor assembly was placed under a bell jar, the internal atmosphere replaced with tank nitrogen, and the mixture blended for five minutes. The emulsion was immediately transferred to a sealed quart container, and held at 25° F. until needed. The above method was termed Blending Procedure I and was used for all experiments with the individual wet and dry rendered lards. To provide uniformly processed test material, samples containing zero moisture were also given the blending treatment.

With the composite lards the blending procedure was altered (Blending Procedure II). The lard was filtered, before processing, in a Seitz filter (K-2 paper) to remove suspended material that might encourage growth of micro-organisms. All blending was done in a 40° F. constant temperature room. Waring Blendors were run in air rather than in nitrogen, and the blended samples were chilled at 30° F., instead of at 25° F. This second

procedure appeared to be more satisfactory than the first and duplicate tests on stability of the processed materials checked more closely.

The effect of the presence of water on the activity of antioxidants representative of those permitted for use in lard by the Canadian Food and Drugs Act (1947) was investigated. (The stabilizers listed in Table III were tested in all six experimental lards, which were adjusted to zero and 1.5 or 1.6% moisture. Some of the antioxidant concentrations (0.5%) were higher than would be used in actual practice: the Act permits the addition of only 0.2% of stabilizing materials, either singly or in combination; moreover, 0.5% gum guaiac or lecithin gives a marked increase in lard color and affects flavor adversely. However, it was considered desirable for comparative purposes to use the larger quantities in initial tests. Citric acid and alpha-tocopherol were used at several levels; low optimum concentrations for these antioxidants have been noted (13). The water content of the wet lard was chosen to be definitely higher than that encountered in commercial lard (less than 1%), but not so high as to facilitate the growth of micro-organisms. Antioxidants were added prior to blending.

All samples were stored at 90° F., to approximate severe shelf storage conditions, and to permit fairly rapid deterioration of the lard while maintaining it in an emulsified state. At each sampling the contents of each jar was stirred thoroughly with a stout glass rod and approximately 10 gm. removed and placed in a sealed container, which was held at −40° F. until chemical measurements could be made.

Measurements

Determination of moisture by the vacuum oven method (1) was impractical at moisture contents higher than 1% because of spattering and the lengthy heating required. The higher moisture values were therefore calculated from measurements of the saponification numbers of the lard samples (1).

There was some doubt as to the suitability of different assessments of rancidity, since the effect of high water levels on the chemical tests was not known. Peroxide oxygen and alpha-dicarbonyl values were determined, since these were known to be useful estimates of oxidative spoilage and to be highly correlated with organoleptic ratings (7). Free fatty acid content was also measured, since added water above 3% might increase hydrolytic spoilage by micro-organisms (5). The following changes in the usual methods (7) were made: for the peroxide oxygen procedure, an accurately weighed 1 gm. (± 0.05 gm.) sample was used; and for the alpha-dicarbonyl measurement, the test solution was filtered through a Whatman No. 40 paper before the colorimetric reading was taken.

Samplings were made at two- or three-week intervals. Storage life was estimated as the time in weeks at 90° F. for the lard to attain a peroxide oxygen value of 10 ml. of 0.002 *N* sodium thiosulphate per gm. (7). The statistical significance of these keeping times was assessed by analyses of variance.

Results

Effect of Moisture Content

In a preliminary experiment, single samples of the four selected lards (*A*, *B*, *C*, and *D*) prepared by Blending Procedure I to contain 0, 1.5, 3, 6, and 12% moisture were stored at 90° F. Contrary to expectations, there was no marked increase in free fatty acid content of any of the samples. A count

TABLE I

EFFECT OF DIFFERENT MOISTURE LEVELS ON THE STORAGE LIFE OF SELECTED LARDS AT 90° F.

(Blending Procedure I, under nitrogen)

Water content, %	Storage life, weeks at 90° F.				
	Wet rendered		Dry rendered		Average
	Lard *A*	Lard *B*	Lard *C*	Lard *D*	
Untreated (0.1)	1.1	5.4	3.2	3.9	3.4
0.0	0.7	5.4	3.3	3.8	3.3
0.75	1.9	4.2	4.0	2.3	3.1
1.5	2.5	5.2	2.1	3.8	3.4
3.0	2.3	5.4	3.0	4.0	3.7
6.0	1.3	3.3	2.0	2.2	2.2
12.0	0.2	2.8	2.6	2.6	2.0
Average	1.4	4.5	2.9	3.2	

Necessary differences (5% level of statistical significance):
between averages for different lards, 0.8 week;
between averages for different moisture levels, 1.0 week.

TABLE II

EFFECT OF DIFFERENT MOISTURE LEVELS ON THE STORAGE LIFE OF COMPOSITE LARDS AT 90° F.

(Blending Procedure II, under air)

Water content, %	Storage life, weeks at 90° F.		
	Lard *E*	Lard *F*	Average
0.0	4.5	3.3	3.9
0.2	4.9	2.5	3.7
0.4	4.2	2.9	3.6
0.8	3.8	3.3	3.6
1.6	3.0	3.2	3.1
3.2	4.8	2.9	3.9
6.4	4.5	3.8	4.2
12.8	2.6	1.8	2.2
Average	4.0	3.0	

Necessary differences (5% level of statistical significance):
between averages for different lards, 0.6 week;
between averages for different moisture levels, 1.2 weeks.

for micro-organisms showed less than 10 per ml. in representative samples after 10 weeks' storage. Peroxide oxygen and alpha-dicarbonyl values increased in a fairly regular manner to give induction-type curves, and values for these two tests were closely correlated (r = .96), in agreement with previous findings (7). This trial indicated that spoilage might be followed by determination of peroxide values only, that low moisture levels should be more carefully examined, and that duplicate samples should be prepared for each moisture level.

In a more comprehensive experiment with the same materials, using the same blending technique (I), moisture contents of 0, 0.75, 1.5, 3, 6, and 12% were studied. The storage results indicated a significant reduction in keeping quality at moisture values of 6 and 12% (Table I). All the lards appeared to react to incorporated water in a similar manner, although they differed in initial stability.

TABLE III

EFFECT OF DIFFERENT ANTIOXIDANTS ON THE STORAGE LIFE OF SELECTED LARDS AT 90° F.

(Blending Procedure I, under nitrogen)

Sample treatment	Storage life, weeks at 90° F.				
	Wet rendered		Dry rendered		
	Lard *A*	Lard *B*	Lard *C*	Lard *D*	Average
Antioxidants in dry lard (zero moisture):					
None*	0.7	5.4	3.3	3.8	
0.005% citric acid	0.9	7.3	2.0	5.4	
0.05% citric acid	2.3	9.7	2.3	4.3	
0.5% citric acid	1.8	12.9	2.8	12.6	9.0
0.5% gum guaiac*	44.0	44+	44+	44+	
0.5% lecithin*	11.2	31.0	24.3	28.4	
0.05% alpha-tocopherol	12.7	18.4	13.5	18.0	
0.5% alpha-tocopherol	16.3	9.9	13.3	13.3	
Antioxidants in wet lard (1.5% moisture):					
None*	2.5	5.2	2.1	3.8	
0.005% citric acid	1.8	6.9	3.4	3.4	
0.05% citric acid	1.3	6.5	3.3	4.3	
0.5% citric acid	2.0	6.6	3.8	3.8	6.4
0.5% gum guaiac*	44+	44+	44+	44+	
0.5% lecithin**	—	—	—	—	
0.05% alpha-tocopherol	7.2	12.9	10.4	12.9	
0.5% alpha-tocopherol	9.1	9.3	8.2	10.8	
Average	5.5	10.0	6.3	8.9	

Necessary differences (5% level of statistical significance):
between averages for wet and dry lards, 1.0 week;
between averages for different lards, 1.4 weeks;
between any two samples, 4.6 weeks.
**Not included in calculations.*
***Contained visible mold growth at later storage periods, hence true storage life could not be estimated.*

With the two composite lards (*E* and *F*), using the revised blending procedure (II), the effect of added water was tested at 0, 0.2, 0.8, 1.6, 3.2, 6.4, and 12.6%. The results, shown in Table II, were similar to those of the preceding experiment, except that only the 12% moisture level caused a significant reduction of storage life.

Effect of Antioxidants

Keeping times for selected lards containing antioxidants are shown in Table III. Samples containing 0.5% gum guaiac were very stable and peroxide

TABLE IV

EFFECT OF DIFFERENT ANTIOXIDANTS ON THE STORAGE LIFE OF COMPOSITE LARDS AT 90° F.

(Blending Procedure II, under air)

Sample treatment	Storage life, weeks at 90° F.			
	Lard *E*	Lard *F*	Average	Grand average
Antioxidants in dry lard (zero moisture):				
None*	4.5	3.3	3.9	
0.02% citric acid	6.5	6.1	6.5	
0.2% citric acid	11.9	8.2	10.1	
0.02% gum guaiac	29.4	17.9	23.7	
0.2% gum guaiac*	39+	33.9	–	12.7
0.02% lecithin	8.8	5.4	7.1	
0.2% lecithin	13.7	10.6	12.2	
0.02% alpha-tocopherol	18.9	14.7	16.8	
0.2% alpha-tocopherol	16.2	9.8	13.0	
Antioxidants in wet lard (1.6% moisture):				
None*	3.0	3.2	3.1	
0.02% citric acid	6.4	3.6	5.0	
0.2% citric acid	6.1	3.4	4.8	
0.02% gum guaiac	30.1	17.2	23.7	
0.2% gum guaiac*	39+	39+	--	8.7
0.02% lecithin	5.9	3.3	4.6	
0.2% lecithin	8.2	4.3	6.3	
0.02% alpha-tocopherol	11.7	9.1	10.4	
0.2% alpha-tocopherol	9.0	5.7	7.4	
Average	13.0	8.6		

Necessary differences (5% level of statistical significance):
between averages for different lards, 1.1 weeks;
between grand averages for wet and dry lards, 1.1 weeks;
between averages for sample treatments, 2.0 weeks.
**Not included in calculations.*

determinations were not continued to the limiting value. Wet lard (1.5% moisture) with 0.5% lecithin gave erratic results and contained visible molds at the later samplings. Hence some of the values could not be estimated.

With incorporated antioxidants, all four lards kept better at zero moisture than at 1.5% moisture (Table III). Over all antioxidant treatments, the

average storage life of lards *B* and *D* was longer than that of *A* and *C*. On the whole, alpha-tocopherol gave longer life than citric acid, particularly in dry lard; the difference in effectiveness was greatest in the most unstable lard (lard *A*) and least in the most stable lard (lard *B*). Better results were obtained from 0.05% than from 0.5% of alpha-tocopherol in the better lards (*B* and *D*) but not in the poorer lards (*A* and *C*). No significant difference in the results from the three levels of citric acid was demonstrable, although there was some indication that citric acid was more effective at the higher concentrations in the better (dry) lards. Gum guaiac was the most effective antioxidant at the 0.5% level, with lecithin next (for dry lard). No consistent difference in the results associated with wet or dry *rendering* of the lards was detectable.

In further experiments to test the relative effectiveness of the above stabilizers in composite lards, the results (Table IV) were confirmatory of the earlier experiments. Analysis of variance of the data indicated that, on the average, the two lards differed significantly in storage life, and that the dehydrated samples of both lards kept better than the ones with added moisture. The experiment did not demonstrate any significant difference between the two lards in their response to the antioxidants. The storage life of both lards was definitely prolonged by gum guaiac and alpha-tocopherol, both of which gave a longer storage life than citric acid or lecithin. A somewhat longer storage life resulted from the higher of the two concentrations of citric acid and lecithin tested, whereas with alpha-tocopherol the lower concentration gave the longer storage life.

Conclusions and Discussion

The results emphasize the importance of the nature of the substrate and the concentration of the addend in lard stabilization. Water alone reduced the storage life of lard only at the higher moisture levels (6 and 12%), but the added stabilizers were more effective in dry lard than in lard containing about 1.5% added water, with the exception of gum guaiac, which behaved similarly in the presence or absence of water. At the 0.5% level, lecithin was more effective than alpha-tocopherol, but at the lower concentrations the reverse was true. Alpha-tocopherol showed a low optimum concentration effect, which tended to be obscured with the lards of poorer initial quality. Citric acid, on the other hand, appeared to be more effective at the higher levels of incorporation in the better (dry) lards, but exhibited no concentration effects in the presence of moisture. The stabilization imparted by gum guaiac and lecithin increased with the amount added. Gum guaiac appeared to be the most generally effective antioxidant permitted for use in Canadian lard by the Food and Drugs Act (1947).

The results for the effect of water alone at small concentrations, and for the relative activities of citric acid and gum guaiac in the presence and absence of water are in agreement with earlier findings (6, 8, 10). Optimum concen-

trations for citric acid, lecithin, and alpha-tocopherol have also received earlier study (2, 13, 17). The action of water on the stabilizing power of lecithin and alpha-tocopherol has apparently not been specifically examined heretofore.

Since gum guaiac and alpha-tocopherol are both phenolic in nature, it might be expected that the antioxidant activity of both materials would be reduced in the presence of water (12, p. 174). The undiminished effect of gum guaiac in lard containing water may be ascribed to the complex nature of the guaiac resin: reduction in potency of the contained phenols by water may be offset by hydrolysis of inactive ester or oxy groups to more active structures (17).

As the stabilizing action of citric acid was reduced by water, this action apparently does not depend on ionization. If citric acid is considered as a synergist only, dependent for its activity on traces of naturally occurring phenolic antioxidants (17), its lessened activity in the presence of water may be due in turn to the lessened activity of these phenolic compounds in the presence of water. This is supported by the report that the chief naturally occurring antioxidants in lard are tocopherols (4; 16, p. 18).

The most satisfactory method of preparing a stable, dehydrated butter oil was found to be one that ensured the transfer of a high phosphatide content from the serum to the fat (5). Consequently, the reduction in antioxidant activity of lecithin in the presence of water may be due to a reversal of this effect; i.e., transfer of phosphatide to the aqueous phase.

The most evident demonstration of an optimum antioxidant concentration occurred with alpha-tocopherol. With both lecithin and alpha-tocopherol excess amounts are detrimental because these materials are vulnerable to oxidation, and their oxidation products accelerate spoilage of the fat (16, p. 19; 17). The optimum concentration of alpha-tocopherol was higher with the poorer lards presumably because these initially contained more pro-oxidant materials that destroyed more of the added antioxidant. The optimum concentration of citric acid may be related to its synergistic action (17); addition of further citric acid after maximum synergistic effect was obtained would be useless.

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A COMPARATIVE STUDY OF TEN ELECTRICAL METERS FOR DETERMINING MOISTURE CONTENT OF WHEAT[1]

I. HLYNKA[2], V. MARTENS[3], AND J. A. ANDERSON[4]

Abstract

Ten electrical moisture meters were tested with 159 samples of Canadian hard red spring wheat, of Grades 1, 2, 3, and 4 Northern, representing a moisture range of 11 to 17%. The two-stage vacuum oven and Brown–Duvel methods were used as bases of comparison. Regression equations, standard errors of estimate, and data on temperature effects are reported. The standard error of estimate of vacuum oven results was 0.15% for the Brown–Duvel method, 0.23% for the Tag–Heppenstall meter, and 0.28% for the Universal meter. Other meters had higher errors of estimate.

In 1934, four electrical meters for determining the moisture content of grain were studied in this laboratory (2, 3, 4). Of these, the motor-operated Tag–Heppenstall meter was found to be the most accurate and has since been used in the Inspection Branch of the Board of Grain Commissioners for preliminary tests of moisture content. The results are accepted for samples having moisture contents 0.3% below the maximum limit for straight grades. In normal years about 90% of all samples enter this category. The remaining samples are retested by the Brown–Duvel oil-distillation method and are graded straight, tough, or damp, in accordance with the results of this test.

Since 1934, and particularly within the last two or three years, a number of new meters have been placed on the market. The possibility that one or more of these might prove useful at some stage of the grain marketing process in Canada merited investigation. Accordingly, through the courtesy of the manufacturers, which is gratefully acknowledged, models of the meters were borrowed for the study reported in this paper. Names, manufacturers, and countries of origin of the meters, are listed below:

Name	*Manufacturer*	*Country*
Universal Moisture Tester Model 4A No. 59	R. H. Nichols Ltd., Toronto	Canada
G.R.L. Moisture Meter	Grain Research Laboratory, Winnipeg.	Canada
Tag–Heppenstall Moisture Meter S-3604	C. J. Tagliabue Corporation, (N.J.), Newark, N.J.	United States
Tag–Dielectric Moisture Meter S-Cm-202	C. J. Tagliabue Corporation (N.J.), Newark, N.J.	United States

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[2] *Chemist.*
[3] *Senior Technician.*
[4] *Chief Chemist.*

Patterson Moisture Meter Type 100A S-4	C. J. Patterson Company, Kansas City, Mo.	United States
Steinlite Moisture Meter S-9894	Fred Stein Laboratories, Atchison, Kansas.	United States
Mullard Moisture Meter Type E910 No. RT-279	Mullard Electronic Products Ltd., Shaftesbury Ave., London.	England
N.P.L. Moisture Meter No. 28145	Baldwin Instrument Co. Ltd., Dartford, Kent.	England
Marconi Moisture Meter Type TF842 No. 705713	Marconi Instruments Ltd., St. Albans, Herts.	England
Toplis–Simpson Moisture Meter S-1300/08	Toplis, Simpson & Co. Ltd., Wembley, Middlesex.	England

Perhaps it should be mentioned at once that some of the meters are still under development, so that parts of this paper may be out of date before it is published. For instance: the Universal meter that was studied had a screw press, but a model with a hydraulic press has since been produced and may finally be preferred; the G.R.L. meter, an experimental model, is not yet being manufactured; the Patterson meter, which is primarily designed for flour, is now used with ground rather than whole wheat; and improved models of the Toplis Simpson and Marconi meters have been developed since the present investigation was completed. Moreover, news has recently been received of other meters that may shortly be on the market. However, since further investigations are not planned for the immediate future, there is no point in delaying publication of this paper.

Two main investigations are described. The first involved calibration, with 159 samples of wheat at 72° F., of all meters and the Brown Duvel method in terms of the vacuum oven method. The second dealt with correction factors for temperature, and was made with four samples of different moisture contents at five temperature levels. Materials and methods for both studies are described in the next section. Data for the comparison of the Brown-Duvel and vacuum oven methods are then given. Following sections deal with the operation of the meters and then with the individual meters in order of their estimated precision. A final section contains a general discussion of the results.

Materials and Methods

Materials

One hundred and fifty-nine samples of Western Canadian hard red spring wheat, each taken from an individual carlot shipped during the 1947-48 crop year, were obtained through the co-operation of the Inspection Branch of the Board of Grain Commissioners. The series was selected so as to obtain a relatively uniform distribution of moisture contents between 11.5 and 17.5%

and of bushel weights between 55 and 65 lb., and was restricted to Grades 1, 2, 3, and 4 Manitoba Northern. Individual samples weighed about 7.5 kgm. and were received and kept in 1-gal. tin cans with small screw stoppers.

Calibration Study

All meter tests were made by one man with an assistant to help with the subdividing and weighing of the samples. Moreover, this team made a preliminary study with 50 samples in order to familiarize itself with the operation of the meters. The work was done in a small, 14 by 11 ft., laboratory automatically maintained at 72° ± 0.5° F. As the air in this laboratory circulates rapidly, and as the control cycle is approximately five minutes, such minor variations as occur in temperature are too rapid to be effectively transferred to equipment or samples. Throughout the investigation, voltage of a-c. current may have varied between 114 and 118 v., but tests showed that none of the meters were affected by variations of as much as ± 10 v.

All meters were tested with one of the 159 main samples before starting tests with another. The 7.5 kgm. sample, which had been kept in the constant temperature laboratory for at least two days, was first mixed by passing it four times through a Boerner sampler and was subsequently divided into 64 subsamples of 115 gm. each. Two subsamples were then allotted at random to each meter, to the Brown-Duvel method, and to the vacuum oven method. When a meter required more than 115 gm., additional pairs of subsamples were allotted to it and composited to make larger subsamples. Single readings on duplicate subsamples were made with each meter, and the order of testing the meters was randomized. About 45 min. was required to prepare subsamples and to take all meter readings on one main sample.

Temperature Study

Four large samples (35.5 kgm.) were obtained with the following average moisture contents: 16.0, 14.8, 13.6, and 11.5%. Each of these was thoroughly mixed in a McClellan mixer and then subdivided with the Boerner sampler into five 7.5-kgm. samples, one of which was used at each of five temperatures, 50°, 60°, 70°, 80°, and 90° F. The procedure described above was used for obtaining subsamples and making the meter readings.

The temperature of the laboratory was set at 50° F. for the first working period and was subsequently raised 10° F. for each of four additional working periods. After the temperature had been raised by 10° F., the next working period was delayed about 40 hr. to ensure that meters and samples reached equilibrium at the new temperature. Tests showed that no significant loss of moisture from the samples occurred during the 11 days required for this study.

Vacuum Oven and Brown–Duvel Methods

A two-stage vacuum oven method (2) was employed as a primary standard procedure, and determinations were started on the day that meter readings were made on the sample. The duplicate subsamples allotted to the vacuum

oven were air-dried at room temperature in trays for two days during which the moisture content was reduced to about 9%. After grinding in a Wiley mill with a 1 mm. sieve, duplicate 2-gm. samples of the meal were subsequently dried overnight in the vacuum oven at 100° C. Four results were thus obtained for each of the 159 main samples. The standard error of the mean of these four determinations was 0.047%.

The Brown–Duvel tests were made by an experienced operator using a carefully standardized, six compartment, electrically heated machine, with a 100 gm. sample and a cutoff temperature of 185° C. The standard error of the mean of tests on duplicate subsamples was 0.05%. It was the intention

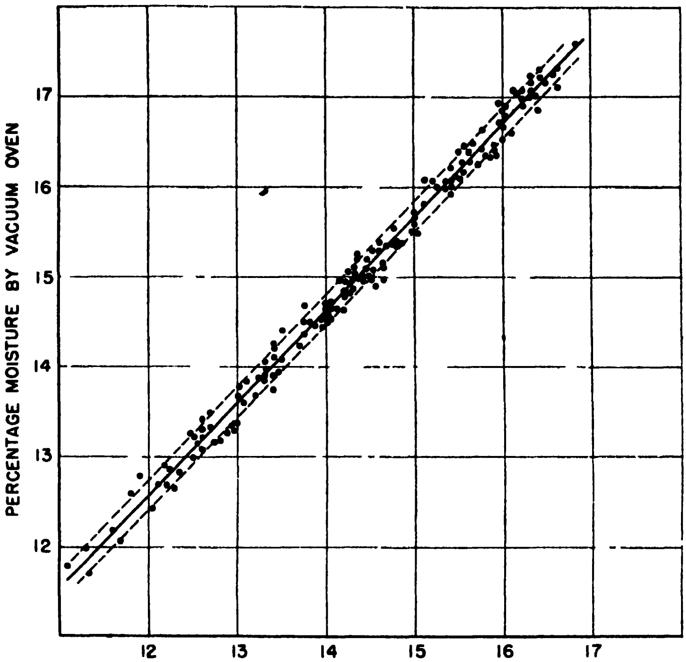

FIG. 1. *Scatter diagram showing the relation between moisture contents determined by the vacuum oven and Brown-Duvel methods for 159 samples of hard red spring wheat.*

to make Brown–Duvel determinations on the same day as meter readings, but this did not prove feasible. Accordingly, some samples were held in glass jars with screw caps for several weeks; but a check of sample weights showed that no appreciable change in moisture had occurred during this period.

Fig. 1 is a scatter diagram in which oven results are plotted against Brown–Duvel results for the 159 samples of hard red spring wheat. This diagram shows that the 159 samples covered the range of moisture from 11.5 to 17.5% relatively uniformly. Since the dots fall relatively close to the regression line, the agreement between the two methods is shown to be good. The error of prediction of vacuum oven moistures from Brown–Duvel results

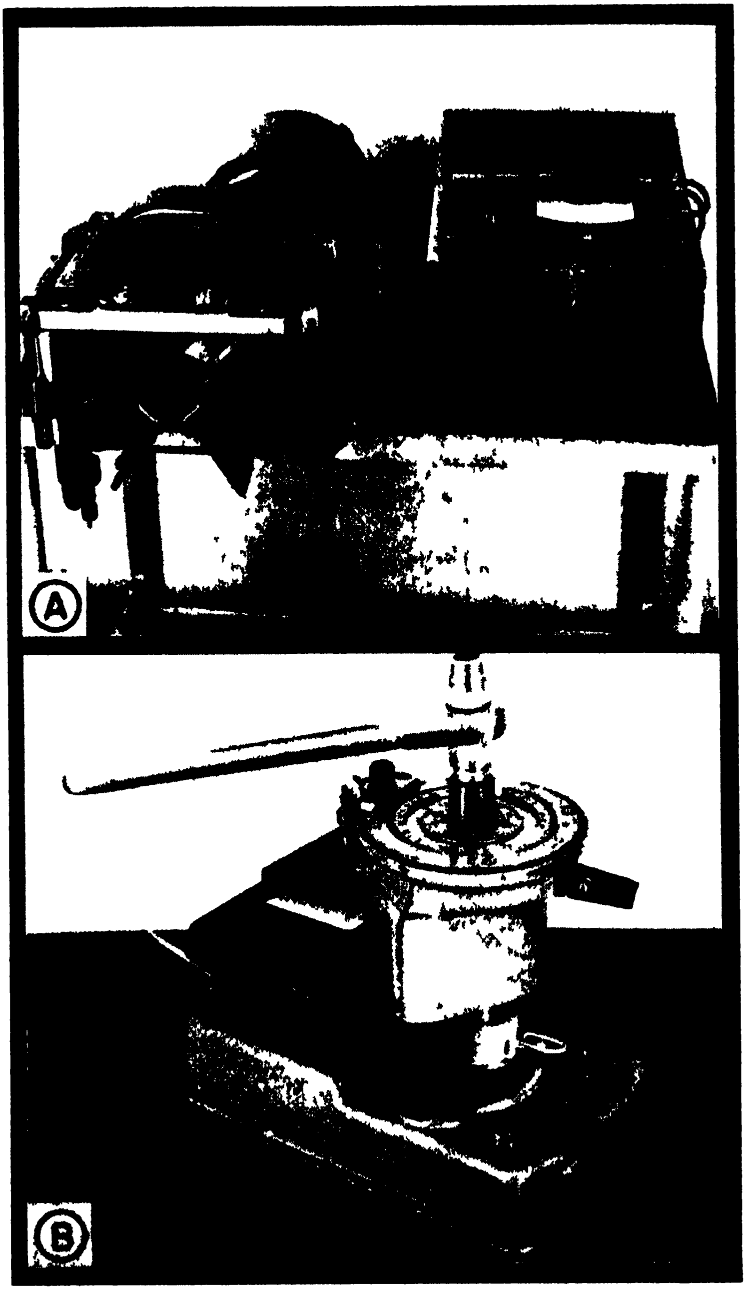

FIG 2 *Photographs of (A) Tag–Heppenstall Meter and (B) Universal Meter*

proved to be 0.15% moisture, and dotted lines corresponding to this deviation about the regression line are also shown in the figure. It may be mentioned, in passing, that the error of estimate for the Brown–Duvel method proved to be considerably lower than that for any of the electrical meters.

Two further points should be noted. Firstly, the regression line in Fig. 1 does not make an angle of 45° with the axes; the regression coefficient is 1.03 rather than 1.0. This means that, by comparison with vacuum oven, the Brown–Duvel method underestimates moisture content by an amount that increases with increasing moisture level. And secondly, the average moisture for the 159 samples was 15.0% by the vacuum oven, whereas it was 14.4% by the Brown–Duvel method. This discrepancy arises from the fact that the Brown–Duvel method was originally calibrated against an air-oven method. Cook, Hopkins, and Geddes (2) obtained similar results. In spite of these faults, the Brown–Duvel method gives precise results that can readily be converted to vacuum oven moisture by means of the regression equation $y = 1.03x + 0.14$ where y is the vacuum oven moisture and x is the Brown–Duvel moisture. It should be added that no correction for the temperature of the grain is required with the Brown–Duvel method, whereas all electric meters have relatively large temperature coefficients.

Operation of the Meters

Photographs of all the meters except the Marconi and the Toplis–Simpson are shown in Figs. 2 and 3. No attempt will be made to describe the circuits in detail, but notes on the principal differences in design and operating technique are given in this section.

The Tag–Heppenstall and Universal meters measure the conductance or resistance of the grain and can be calibrated in ohms. All other meters make measurements that are functions of the change in capacitance of a condenser when grain is introduced as a dielectric. In three of the meters, the Universal, G.R.L., and Patterson, the characteristics of the circuits are such that no standardization of them is required. The remaining meters have convenient provisions for standardizing or balancing the circuits, and this operation must be undertaken before a series of tests is made. All meters require a-c. current of either 110 or 220 v., except the Toplis-Simpson and Marconi meters, which have batteries, and the Universal meter, which requires neither power nor batteries. The Universal meter has a built-in armored thermometer, but with all other meters the temperature of the grain must be read with a thermometer before starting the test.

Resistance Type Meters

In the Tag–Heppenstall meter (Fig. 2, A), two corrugated steel rolls serve as electrodes; one is motor-driven and the other idles. Grain is poured into the hopper above the rolls and is partially crushed as it passes between them. A selector switch is turned to one of eight positions that control the range

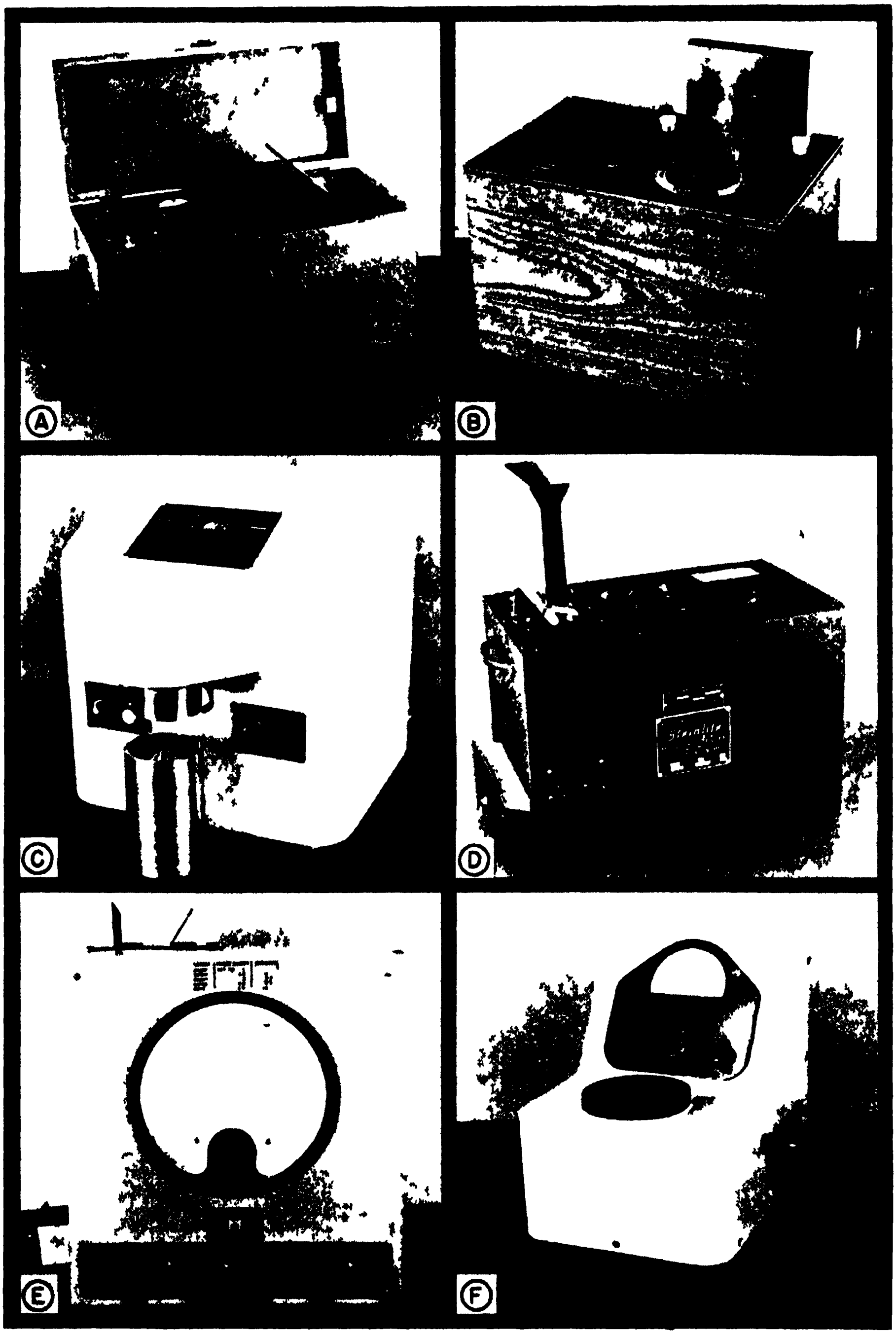

FIG 3 *Photographs of (A) Tag–Dielectric (B) G R L (C) Patterson (D) Steinlite (E Mullard and (F) N P L moisture meters*

of values indicated by the galvanometer, and the position of the galvanometer pointer is read. Charts are provided for converting readings to moisture contents. Only about 10 to 20 sec. is required to make a reading.

The spacing between the rolls is critical and must be maintained with shims when the rolls wear appreciably as a result of passing several thousand samples through them. An increase of 1/1000 in. in the spacing reduces moisture readings by about 0.03%. The same spacing is used for wheat, barley, and oats, but a thick shim must be introduced to narrow the spacing for testing flax. A different set of rolls with larger corrugations is used for corn.

In the Universal meter (Fig. 2, B), a hand-driven megger establishes a voltage across a sample of compressed grain, and electrical resistance is indicated on an ohmmeter of the dynamometer type. The instrument thus requires neither batteries nor power supply.

A test is made on a 10 gm. sample weighed to the nearest kernel. This is transferred to a steel cup with a cylindrical plastic lining (internal diam. 2 in.). The cup is placed beneath the ram of a screw press operated with a ratchet wrench, and the grain is compressed to a thickness of 0.220 in., which is indicated by a micrometer device on the ram. The megger is then cranked rapidly and the meter and temperature are read. After the test, which requires about 1.5 min., the partially crushed grain can be readily removed from the cup with a screw driver.

Circular sliding scales for converting temperatures and meter readings to moisture content are provided on the top of the press. But the calibration does not appear to be correct for wheat (see next section) and would not be expected to suit all types of grain and seeds. Accordingly, conversion charts will probably be required. The meter can be used with a variety of grain and seeds, such as flax and rape, without change in adjustment. All that is required is that the weight of sample and the thickness of the pressed layer be adjusted to suitable values for each seed.

Dielectric Type Meters

All the dielectric meters are operated in much the same way in that a sample is introduced into the cell, certain switches, push buttons, or dials are manipulated, and a reading is taken either from a dial or from an indicating instrument with pointer and scale. Single tests can be made in about 1 to 1.5 min. Photographs of six of the meters are shown in Fig. 3: (A) Tag-Dielectric; (B) G.R.L.; (C) Patterson; (D) Steinlite; (E) Mullard; and (F) N.P.L. The principal differences between these meters are noted below. Most of the meters have already been described: G.R.L., (6); Marconi (1); N.P.L., (5); and the remainder in advertising literature.

In order to obtain uniform packing of the sample within the test cell, loading hoppers with spring or trip release mechanisms are provided in the G.R.L., Steinlite, Mullard, and Marconi meters. Each of these has provision for

dumping the tested sample into a drawer for removal. A special funnel with a spring-operated release is provided for loading the cell of the Patterson meter. And this and the remaining meters have removable cells that are readily emptied.

No loading hoppers are provided for the Tag–Dielectric, N.P.L., and Toplis–Simpson meters. Tests showed that uniform loading of the cells of the last two meters did not improve the results obtained with them. But uniform loading did improve the results obtained with the Tag–Dielectric meter, and this meter was therefore used with the Steinlite hopper.

The weights of wheat required for single tests with the dielectric meters are as follows: Tag–Dielectric, 260 gm.; G.R.L., 190 gm.; Patterson, 20 gm.; Steinlite, 150 gm.; Mullard, 100 gm.; N.P.L., about 300 gm.; Marconi, about 150 gm.; and Toplis–Simpson, about 150 gm. With the last three meters, the cell or hopper is merely filled level with the top. With all other dielectric meters, the sample must be weighed.

The Patterson meter has a novel feature consisting of a servo-mechanism that balances the circuit. After the loaded cell is clipped in place, a button is pushed, and the operator has only to read the position of a scale when the servo-mechanism stops.

Results

Sampling error, in terms of the electrical properties measured, proved to be negligible; each meter gave almost identical results for duplicate subsamples. Accordingly, the statistics reported below relate to the mean values given by the meters and by the vacuum oven for each of the 159 main samples. Scatter diagrams, regression equations, standard errors of estimate of moisture content (vacuum oven) from meter readings, and graphs showing the results of the temperature study, are presented for the more precise meters, and corresponding data are summarized for the remaining ones.

Tag–Heppenstall Meter

The Tag–Heppenstall meter can be most conveniently calibrated in ohms. It has a range from 2000 ohms to about 85 megohms, which corresponds to a moisture content of wheat ranging from 10 to 24%. An inverse logarithmetic relation exists between the resistance (R) of the grain in ohms and percentage moisture content. Accordingly, a direct linear relation is obtained by plotting moisture content against $10 - \log R$. Fig. 4 shows this plot for the 159 samples tested. The slope of the regression line is 2.47 and the standard error of estimation of moisture content (vacuum oven) from the meter readings is 0.23% moisture. The dotted lines drawn 0.23 percentage units above and below the regression line thus represent the error of estimate and include about two-thirds of the points. Points lying farther from the regression line represent samples whose moisture contents would be least accurately estimated by the meter on the basis of the regression equation. Errors of as much as $\pm$ 0.7% can occasionally occur.

The regression equation obtained for the Tag–Heppenstall meter takes the form $y = bx + c$, where y is the moisture content, x is the meter reading in log ohms (or 10–log ohms), b is the regression coefficient, and c is a constant. The value for c is a function of the sharpness of the corrugation on the rolls and the space between the rolls. Accordingly, exactly the same equation is not obtained for two meters unless the rolls and spacing are identical. For

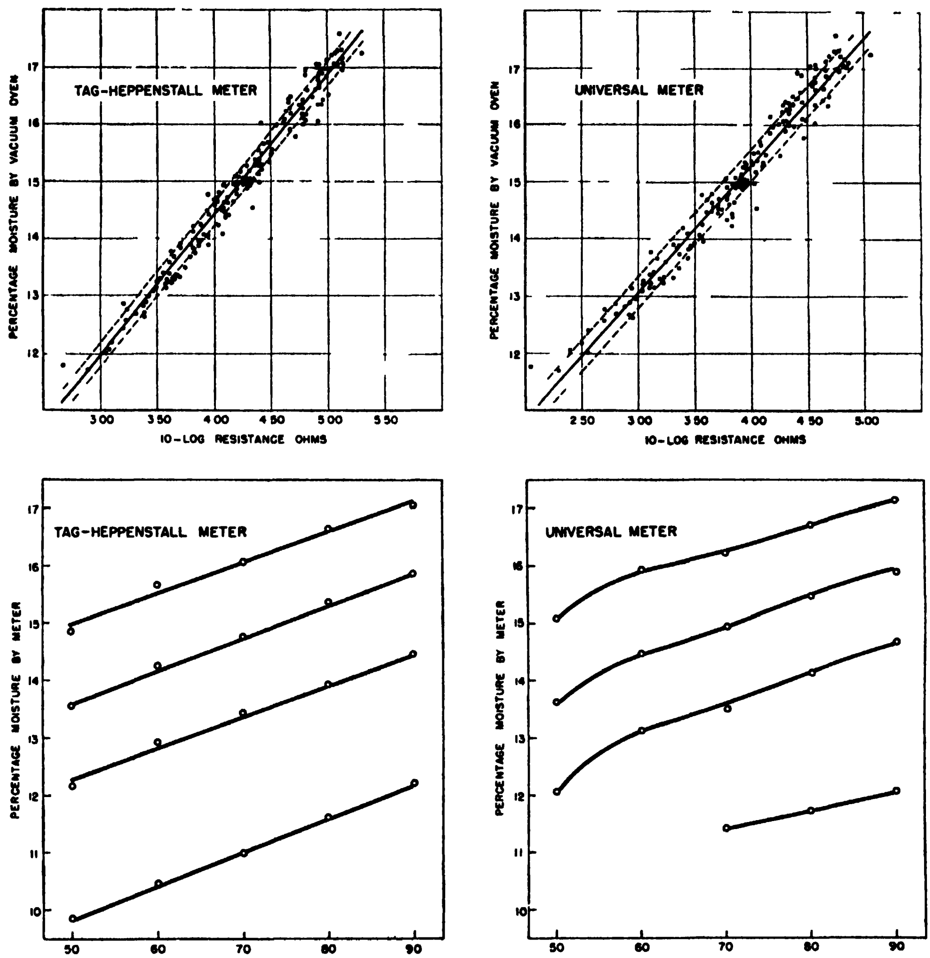

FIG 4 *Scatter diagrams showing the relations between moisture content (vacuum oven) and 10—log resistance (ohms) for Tag–Heppenstall and Universal meters Curves showing the relations between percentage moisture by meter and temperature for the two meters.*

this reason, a direct comparison of the equation obtained in the present study and that obtained in a similar study (3), made in the laboratory 15 years ago, is not feasible. However, indirect comparison shows that if both meters had been adjusted to give identical readings for grain of 15% moisture, results obtained with the two meters at 11 or 17% moisture would have differed by 0.03%. This difference is negligible for all practical purposes.

As the rolls on the meter wear and the spacing between them increases, moisture content is progressively underestimated. This error can be corrected by shimming when a decrease in spacing of 1/1000 in. raises the meter reading by the equivalent of about 0.03% moisture. However, the most accurate corrections for wear cannot be made merely by re-establishing a constant spacing between rolls. For experiments have shown that the spacing required to maintain the calibration also depends on the sharpness of the corrugations; as this decreases, compensation must be afforded by additional decrease in spacing. These minor difficulties are readily overcome in practice by calibrating meters periodically against the vacuum oven, or other standard method, and shimming to re-establish the calibration.

The results for the study of the effect of temperature on the Tag–Heppenstall meter are shown in Fig. 4. The four curves, representing samples of different moisture contents, are linear and parallel. This represents an ideal situation in which a single correction factor covers the temperature range (50° to 90° F.) and moisture range (11.5 to 16.0%) investigated. It seems probable that this generalization will hold for wider ranges. The regression of moisture on temperature is 0.056% per ° F. This is lower than the value of 0.068% established in the earlier study (3), and since this was obtained by study of about 30 samples, rather than four, it is considered the more reliable figure.

Universal Meter

Although the megger of the Universal meter is provided with an arbitrary scale, this can readily be converted to ohms. The range of the megger is from 5,000 ohms to 50 megohms, which corresponds to a moisture range of about 11.5 to 18%. The scatter diagram for moisture content (vacuum oven) against $10 - \log R$ (Fig. 4) shows an essentially linear relation represented by the regression equation, $y = 2.24x + 6.37$. The standard error of estimate is 0.28%.

Since the Universal meter shows considerable promise, it was also calibrated against the Brown–Duvel method. The linear regression proved to be $y = 2.15x + 6.06$, and the standard error of estimate was 0.27%. To make a direct comparison of the arbitrary megger scale readings and the Brown–Duvel method, a fourth degree polynomial was fitted to the points. The reduction in the standard error by this method of calculation was negligible. A chart for converting readings on the arbitrary megger scale to moisture contents, based on the fourth degree equation, has been prepared.

Results for the study of temperature effects are shown in Fig. 4. The curves suggest that a single correction factor (0.045% per ° F.) is applicable within the range of 60° F. to 90° F. and of 15.7% down to 13.0%, and possibly to 11.0%, of moisture. There is an indication, however, that the slopes of the curves change below 60° F., and that different corrections would be required below this temperature level. Further investigation is required to establish this point.

The manufacturers have calibrated the instrument, and have provided engraved scales on the top of the instrument from which the operator can readily obtain the moisture content when the megger reading and temperature are known. This calibration does not agree with those obtained in the present study either for the meter and the vacuum oven or for the meter and the Brown–Duvel method. By comparison with our vacuum oven data, the manufacturers' calibration is lower by an average of 0.75%; by comparison with our Brown–Duvel data, it is high at low moisture levels (11 to 13%) and low at high moisture levels (14 to 17%). In view of the large number of samples used in the present study, and the fact that all these were taken from commercial carlots of grain, it seems probable that the manufacturers' calibration is erroneous.

Dielectric Type Meters

Scatter diagrams for six of the dielectric type meters are shown in Fig. 5. The calibration equations and standard errors of estimate of moisture content (vacuum oven) are given in Table I. Diagrams for the Tag–Dielectric and

TABLE I

CALIBRATION EQUATIONS AND STANDARD ERRORS OF ESTIMATE FOR ELECTRICAL MOISTURE METERS

Meter	Unit of measurement	Calibration equation*	Standard error of estimate, moisture, %
Tag–Heppenstall	10 – log of resistance, ohms	$y = 2.47x + 4.54$	0.23
Universal	10 – log of resistance, ohms.	$y = 2.24x + 6.37$	0.28
Tag-Dielectric	Meter reading	$y = .109x + 3.62$	0.35
G.R.L.	Meter reading	$y = .132x + 10.07$	0.36
Patterson	Meter reading	$y = .186x + 7.29$	0.41
Steinlite	Meter reading	$y = .106x + 11.09$	0.44
Mullard	Meter reading	$y = .876x + 10.88$	0.48
N.P.L. Switch Pos. 1	Meter reading	$y = .116x + 14.57$	0.50
N.P.L. Switch Pos. 3	Meter reading	$y = .131x + 9.25$	0.49

**y* = *Vacuum oven moisture.* *x* = *Unit of measurement.*

Patterson meters suggest slightly curvilinear relations especially for moisture contents over about 16%. The N.P.L. meter is provided with a selector switch for changing the range, and diagrams for two ranges are therefore shown.

Results obtained with the Marconi (Model TF842) and the Toplis–Simpson (Model S–1300/08) meters were less satisfactory than those for the other meters. As both companies have substituted new models for the older ones examined in this laboratory, data on the latter are not reported.

Fig. 6 shows the results of the temperature study for six meters. Among these, the G.R.L. meter most nearly approaches the ideal in which all curves are straight and parallel. But the Tag–Dielectric, Steinlite, and Mullard

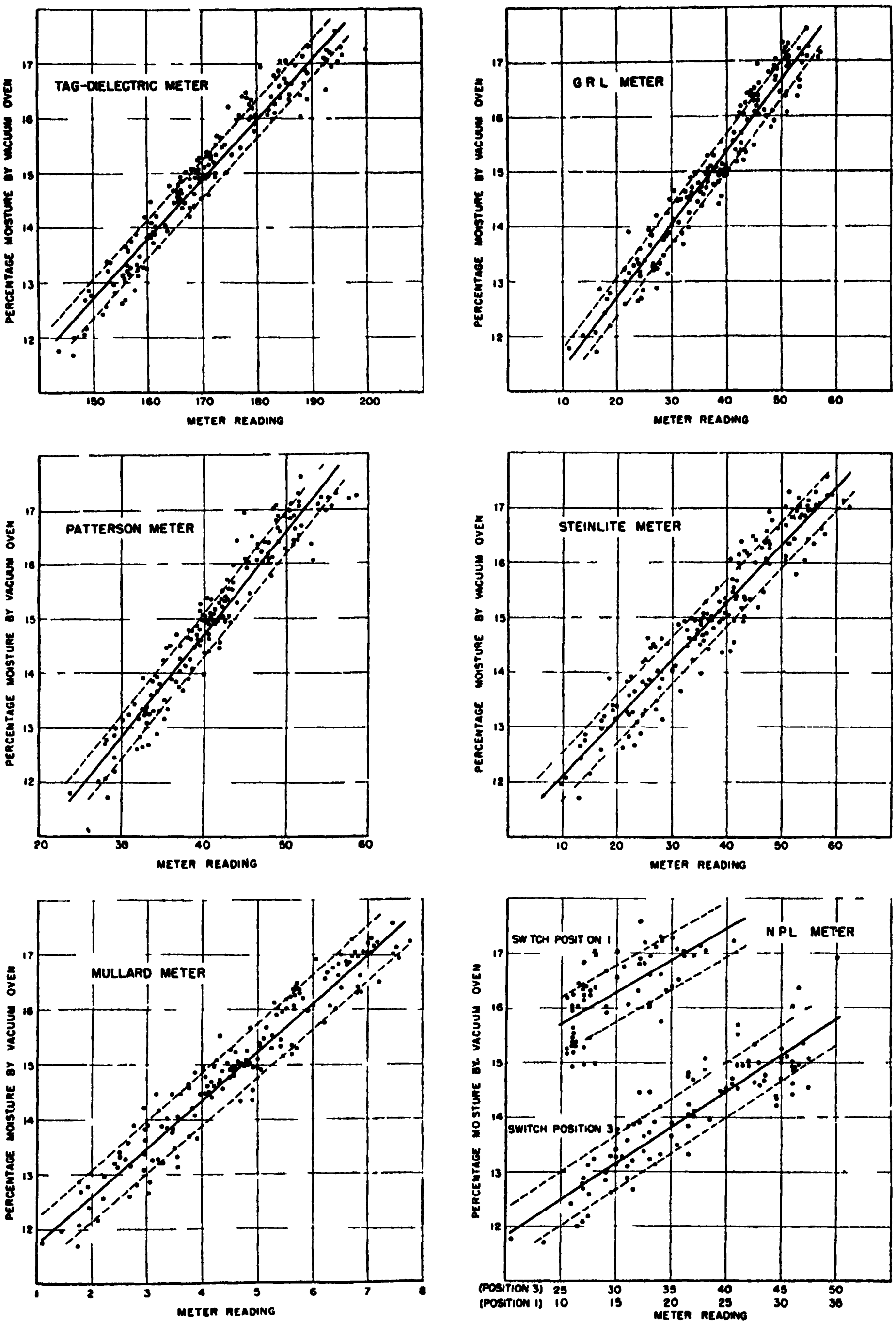

FIG. 5. *Scatter diagrams showing the relations between percentage moisture (vacuum oven) and meter readings for six electrical moisture meters.*

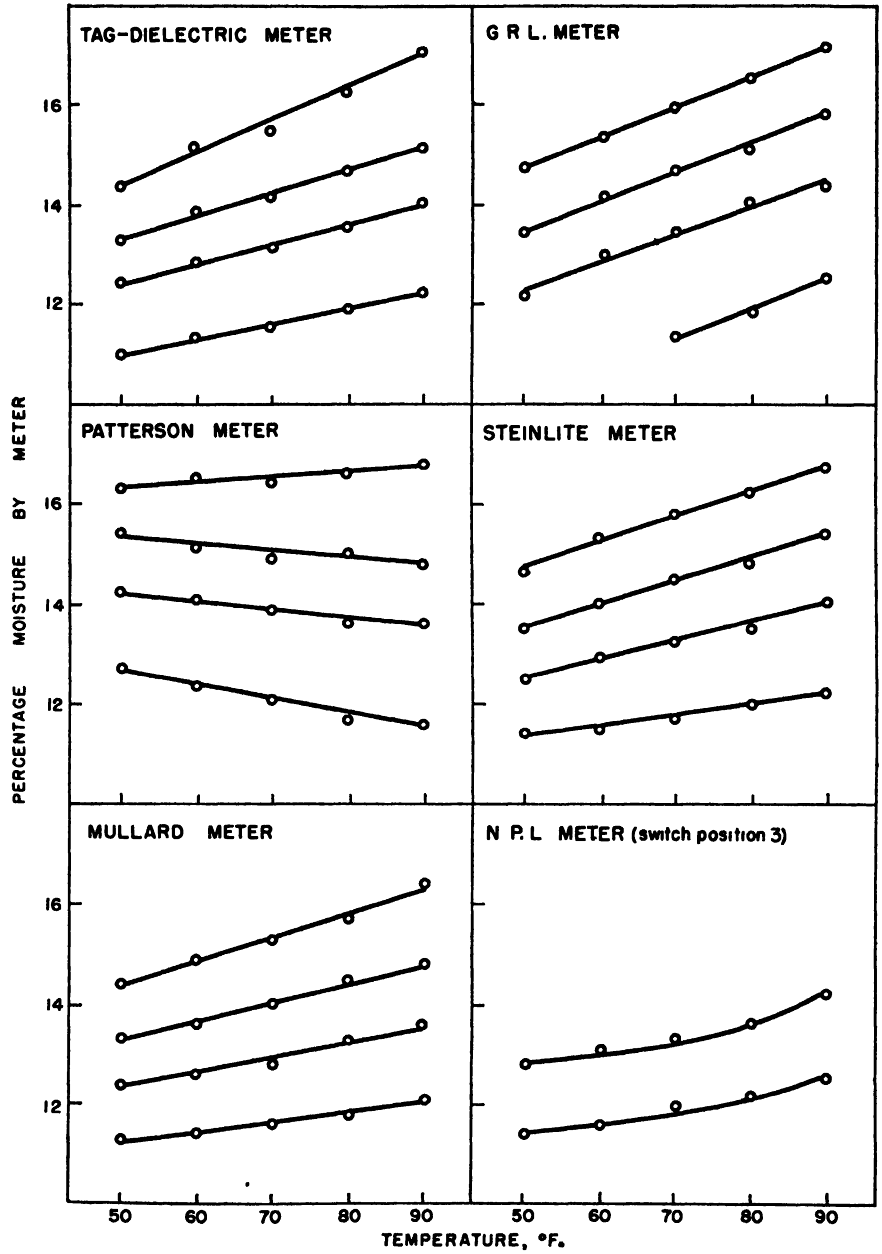

FIG 6 *Curves showing the relation between percentage moisture by meter and temperature for six electrical moisture meters.*

meters show only minor deviations from the ideal. The N.P.L. meter shows slightly curvilinear relations. On the other hand, the Patterson meter appears to require different correction factors for samples of high and low moisture content. In general, however, the adoption of a single temperature correction factor for each meter would introduce errors that are small by comparison with those resulting from the looseness of the relation between moisture content and meter readings.

Discussion

The data reported in this paper relate to single samples of each manufacturer's meter. A question thus arises as to whether a generalized statement can be made about the comparative merits of the meters. For the Tag–Heppenstall and Universal meters, several of which have been tested in this laboratory, some additional information is available. Experience has shown that Tag–Heppenstall meters that are in good working order can be readily adjusted by empirical tests to give results in accordance with a specified calibration. Several Universal meters have also been shown to give uniform results, and there is reason to believe that these meters will retain their calibration during a reasonable working life. Discussions with other chemists suggest that some variation in setting may exist among replicates of some other instruments. Accordingly, the calibration equations reported in this paper may not be accurate for all examples of each meter. And moreover, these calibrations apply only with Canadian hard red spring wheat and would not be expected to give the most accurate results for wheats of other classes. Any laboratory purchasing a new meter should check the calibration and recalibrate if this seems necessary.

There is also the question of whether repetition of this study would place the meters in the same rank order of accuracy. The statistical significance of differences between standard errors of estimate cannot be computed from the data for a single study. But experience suggests that it is of the order of 0.3 percentage units or less. On this basis, the Tag–Heppenstall meter yields the most accurate estimates of moisture content and is followed by the Universal meter. The remaining meters fall into four groups listed in order of accuracy as follows: Tag–Dielectric and G.R.I.; Patterson and Steinlite; Mullard and N.P.L.; and Marconi and Toplis–Simpson.

Even the best of these meters will give an erroneous estimate of the moisture content of a considerable proportion of any series of samples. This is to be expected. The meters measure electrical properties of the grain, which are functions of several other properties and conditions of the samples of which moisture content is only one, though the most important. Among these other factors, the distribution of the moisture is known to affect electrical properties. Accordingly, a calibration established for the average distribution of moisture in normal samples is not accurate for samples in which the distribution is abnormal because the grain is freshly harvested, recently tempered, or recently subjected to rapid drying. The packing of the sample in the test

cell also has a major effect on electrical properties, and most meters therefore have loading hoppers designed to reduce this source of variation. For these and other reasons, not yet fully investigated, an accurate prediction of moisture content by electrical methods is not likely to be achieved by any meter for all samples in any random series.

Besides being the most accurate, the Tag–Heppenstall meter provides the most rapid tests, has a uniform temperature correction coefficient, and requires no balance for weighing the sample. These advantages are offset in part by the change in calibration as the rolls wear; though the original calibration can be re-established by simple empirical methods. In addition to its standing of second in accuracy, the Universal meter has the decided advantage of requiring no batteries or external source of current. Among the other meters, several have minor advantages of various kinds, but these are not considered sufficient to offset the greater accuracy of the two resistance types.

Acknowledgments

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MILD OXIDATION OF ALKALI LIGNINS[1]

BY R. A. V. RAFF[2] AND G. H. TOMLINSON II[3]

Abstract

Following the discovery that the reinforcement of GR-S rubber by alkali lignins is greatly enhanced if the lignins, prior to their coprecipitation with the latex, are subjected to oxidation, the reaction of alkali lignins with oxygen and the properties of oxidized lignins were studied. It was found that particularly the melting points of the lignins and their lyophilic properties are increased by continued oxidation. This suggested that these two properties are mainly connected with, and possibly responsible for, the reinforcing capacity of the oxidized lignins in the rubber, which in turn is correlated with particle size, surface area, and adsorptive power. It could also be established that, providing definite coprecipitation conditions are maintained, a well defined oxidation range exists, over which lignins display optimal reinforcing properties.

Introductory Remarks on the Importance of Oxidation Studies on Alkali Lignins

The early stages of development work at Howard Smith Paper Mills Limited on the use of alkali lignin in plastics have shown that the recovery and separation of the lignin from black liquor should be carried out under conditions such as to minimize reaction of the lignin with oxygen from the air. Progressive oxidation was found to increase the lyophilic properties of the wet lignin. This was undesirable from the standpoint of filtering and drying. It also increased the melting point and reduced the flow properties of the dry lignin. This made the latter less suited for molding purposes.

On the other hand, in joint work with Polymer Corporation, Sarnia, Ontario, on the use of alkali lignin as a reinforcing agent for GR-S rubber, it was discovered that reinforcement was greatly enhanced with increasing oxidation (4, 5).

It was thus realized that the reaction of alkali lignins with oxygen would have to be investigated and the properties of oxidized lignins studied. It should be pointed out that the investigation reported here does not include the oxidation of lignosulphonic acids, i.e., of waste sulphite liquor, nor the formation of vanillin.

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Contribution from the Research Department of Howard Smith Paper Mills Ltd., Cornwall, Ontario.
Paper presented before the Wood Chemistry Section of the Canadian Pulp and Paper Association, in Niagara Falls, on June 3, 1949.

[2] *Research Chemist, now Senior Fellow at Mellon Institute, Pittsburgh, Pa.*
[3] *Research Director.*

Reference to Previous Publications in Relation to the Present Problems

As far as the earlier literature on the oxidation of alkali lignin is concerned, the well known books of Fuchs, and Freudenberg, and the article of Max Phillips in "Chemical Reviews", 1934, adequately cover such work up to about 1934. Phillips, in his monograph, points out that the published results on the oxidation of lignin throw little light on the structure of lignin since, even by "mild" oxidation, complete disruption of the molecule is said to take place, resulting in simple degradation products only. This indeed, also applies to most of the more recent publications. Even in the few cases where milder and more controlled oxidation conditions were applied, the main interest of the investigators was in the low molecular degradation products rather than in the remaining lignin skeleton.

Franz Fischer and coworkers (2) reported as early as 1922 that lignin in the presence of alkali is capable of taking up oxygen, particularly at increased pressures and temperatures, whereby he distinguishes between mild and strong oxidations.

Freudenberg, in his book, expresses the belief that mild oxidation of lignin causes the formation of carboxyl groupings, which render the molecule soluble in alkali, without considerably changing its internal structure. Stronger oxidation, however, is said to always lead to simple degradation products, without the possibility of isolating intermediates.

A few of the more recent papers deal also with the changes in the lignin molecule caused by mild oxidation.

Walde and Hixon (7) found that the reaction of ammonia lignin from oat hulls with alkaline iodine solution could be made quantitative. Iodoform was found among the degradation products, the oxidized lignin itself containing iodine and carboxyl groups. Different preparations of lignins gave different titration values, ranging from 68 cc. of $N/10$ iodine solution per gm. sample for sulphuric acid lignin from aspen to 190 cc. for ammonia lignins from oat hulls. When the latter lignin had been pretreated with Fehling's solution, the titration value decreased to 154.

This indicates that the oxidation values for lignin vary considerably, the actual values depending on the method of preparation and pretreatment of the lignin sample. The amount of copper reduced (3) was not found to parallel the loss in iodine oxidation value. The oxidation of lignin with alkaline solutions was further found by Walde and Hixon to be peculiar in that the methoxyl content decreases from 12.5 to approximately 7.4%, while the iodine entering the molecule accounts for only 1.1% of the decrease.

A valuable contribution to the problem of lignin oxidation was made by Bennett of the Massachusetts Agricultural Experimental Station, in a paper entitled "Some Acidic Properties of Alkali Lignin" (1). The article deals

primarily with the possible role of lignin in the absorption of minerals by plants.

Since Bennett felt that increases in base exchange values of soil organic matter may be caused partly by progressive oxidation, samples of corncob lignin were subjected to oxidation with alkaline iodine solutions. Oxidation values of 172 cc. of $N/10$ iodine per gm. of lignin were obtained, and among the degradation products, iodoform was detected, a finding similar to that of Walde and Hixon. The oxidized lignin appeared to be considerably more highly peptized, and base exchange determinations on the electrodialized product indicated an increase of about 35%, probably due to the presence of carboxyl groups.

A method that could possibly be developed into a procedure for determining the reducing capacity of lignins has been reported recently by Schuerch (6, p. 19). In an attempt to find a method for modifying periodate lignin to render it soluble, oxidations at 20° C. with aqueous chromium trioxide buffered to pH 0.5 seemed to show some promise. After about 17 atoms of oxygen had been taken up per 1000 gm. of lignin, the reaction slowed down and the lignin became soluble in alkali. The precipitated, washed, and dried product consumed only eight atoms of oxygen when subjected once more to the same treatment.

Preparation of Lignins of Varying Degrees of Oxidation

In our own work, the oxidized alkali lignin for use in reinforcing rubbers was generally prepared by heating a solution of the sodium lignin salt in water, or a solution of the acid precipitated lignin in caustic, and bubbling oxygen or air through these solutions. The tendency of these solutions to turn acid was counteracted by the addition of sodium hydroxide during the oxidation.

In the course of this work it was necessary to prepare considerable quantities of oxidized lignin for laboratory and pilot plant coprecipitations with the rubber latex. At various stages in this development the oxidation was carried out in a 40 gal. drum, in a type N Roto-Clone, and in a small tower (40 in. diam., 7 ft. high). Because of the somewhat different methods of air-liquid contact employed, the time required to obtain a lignin of suitable reinforcing properties was found to vary over a considerable range.

Changes in Lignin Characteristics Depending on the Degree of Oxidation

It was considered to be highly desirable to establish physical and/or chemical characteristics of the lignin at various stages in the oxidation that could then be related to the reinforcing properties when the lignin was coprecipitated with rubber. A knowledge of the change of the amount of oxygen consumed, corresponding to any given change in these characteristics, was also considered desirable.

(a) Melting Points

One of the most characteristic changes in property is the increasing melting point that is obtained with isolated lignins that have been subjected to progressive oxidation. This increase in melting point is a fairly satisfactory criterion of the degree of oxidation of a lignin sample, so long as it is kept in mind that other reactions, like chlorination, also raise the melting point of lignin, but do not increase its reinforcing properties.

Some points should be noted regarding the determination of the melting point of lignins, which is somewhat less definite than in the case of most low-molecular, crystalline compounds.

One method of determining the melting point of lignins is carried out in the usual Thiele melting point apparatus, using open capillaries, and cottonseed oil as a heating fluid. The lignin sample is finely ground and predried for about 30 min. in an air oven at 105° C., under which conditions no noticeable oxidation takes place. A small quantity of this lignin is then filled into the capillary, without removal of the sample from the oven. The filled capillary is then attached to a thermometer and inserted in the melting point apparatus, which has been heated previously to around 90° C. From then on, the temperature of the bath is slowly and evenly raised, and the sample observed under strong illumination. Generally, lignin samples show a definite shrinkage at a certain temperature, which is noted. Heating beyond this point causes the lignin in most cases either to show definite melting at a definite temperature, or at least to flow together and to wet the walls of the capillary. The temperature at which either or all of these changes occur is taken as the melting point of the sample, although very often no real melting can be observed. Detailed data of the relation between oxidation and the results obtained by this "open tube method" will be presented later in Table V. It is sufficient to mention now that, for example, for a medium-oxidized lignin (i.e., medium, from the viewpoint of rubber reinforcement) the data observed for shrinkage and melting point, respectively were: 214° C. and 228° C.

In search for a more accurate method of determining melting points of lignins, it was thought that volume changes occurring while the sample is being heated could be more easily followed by covering the sample in the capillary with a small amount of mercury and observing the meniscus of the latter. Somewhat larger tubes were found to be more suitable, in which the dried and finely ground lignin was packed tight to a height of 25 mm. and covered with a column of mercury 10 mm. high.

Attaching this tube to the thermometer, inserting it in the preheated melting point apparatus, and gradually increasing the temperature, reveals in most cases three clearly observable points at which changes occur. The above mentioned, moderately oxidized lignin showed, for example, that the mercury level was first raised by increasing the temperature, but then, at 177° C., it suddenly dropped. This point was marked as "shrinkage". Continued

heating caused the mercury level to eventually rise again, until a point was reached at which the lignin sample in the tube turned jet black and glossy, with signs of wetting the wall of the tube. This point (210° C. in the case noted) was called the melting point by this method. Further heating of the sample led to a slight additional rise in level of the mercury. Then, fairly suddenly, gas developed from the lignin sample, forcing its way as bubbles through the mercury. This, in the present case, took place at 224° C., and seemed to be a sign of decomposition or at least of structural changes in the lignin molecule. Thus, the lignin sample by this method gave three characteristic points.

Experiments with the electrically heated melting point apparatus of the Fisher–Johns type gave only one point, at which signs of melting or fusing of the lignin sample were noted. A slight pressure with a needle on the cover glass made it fairly easy to observe that the sample turned, at 213° C., to a jet-black sticky tar.

A comparison of these results, as obtained on the same lignin by the three methods, is shown in Table I.

TABLE I

COMPARISON OF RESULTS OBTAINED BY VARIOUS MELTING POINT METHODS

Method	Characteristic changes		
Open-tube method		Shrinkage 211° C.	Melting 228° C.
Mercury-covered tube method	Shrinkage 177° C	Turns black 210° C	Gas developed 224° C.
Electric stage method		Melting 213° C.	

It would appear from this table that the point of shrinkage observed by the "open-tube method", the point at which the sample turns black in the "mercury-covered tube method", and the melting point observed by the "electric stage method", take place at approximately the same temperature, whereas the melting point by the open-tube method seems to correspond to the point at which gas development is observed in the "mercury-covered tube method".

This agreement is not always as good as in the example shown. More of these figures will be given in Table V. Particularly in the range of "over-oxidized" lignin (that is, from the viewpoint of rubber reinforcement) the agreement is often very poor, even for results obtained on the same sample by the same observer and the same method, regardless of the method used.

As a routine test it was found best to carry out melting point determinations on the same sample by all three methods and to attempt to obtain the above correlation between them.

One interesting fact has been discovered in the course of these investigations, namely, that lignin gives off gases at its melting point. This has been previously overlooked, since melted lignin samples, on remelting, showed essentially the same melting point, and lignin was thus considered to be a true thermoplastic material. Such conclusions should be reconsidered in the light of these recent findings. This thermodecomposition of lignin, which may play an important role during molding when lignin is used in plastics and laminates, has been made the subject of a separate study, results of which will be reported at a later date.

(*b*) *Filter Time and Water Retention*

Any increase in melting point of lignin that is due to oxidation is normally accompanied by an increase in the lyophilic properties of the lignin. This change in properties can be observed in several ways. For example, if solutions of lignins of increasing degree of oxidation, but of the same lignin content, are precipitated with acid at 90° to 95° C., the slurries will filter more slowly the higher the degree of oxidation of the lignin. Further, the lignin cake containing the more highly oxidized lignin will also hold more water. Corresponding results are obtained when coprecipitates with GR–S latices are involved.

Unoxidized lignin can be precipitated in such a way that a fast filtering precipitate is obtained, at a temperature as low as 70° C. However, oxidized lignin, when precipitated at such a low temperature, is hardly filterable. With such lignins, higher precipitation temperatures should be used in order to obtain a product filterable at a reasonable speed, although even under optimal conditions filtering is always slower than with the less oxidized or the unoxidized lignin sample.

Filter times of samples containing standard amounts of lignins, and precipitated under standard conditions, as well as the water contents of the filter cakes, with or without latex, have been used successfully to characterize lignin samples and to check on the progress of lignin oxidations.

(*c*) *Changes of Viscosity in Solution*

The increase in viscosity due to oxidation of solutions of lignin in cellosolve has already been reported (4, 5). However, the changes observed are too small to form the basis of a routine test.

(*d*) *Changes in Methoxyl Content*

The same applies to the change in methoxyl content, which shows a definite, but small decrease with progressing oxidation, at least in the investigated range.

(*e*) *Reduction of Fehling's Solution*

The fact that lignin preparations reduce Fehling's solution has been observed by Powell and Whittaker (3). There is definite indication that the ability of a lignin to reduce Fehling's solution, as measured by the amount of cuprous

oxide deposited under standard conditions, decreases with increasing degree of oxidation. But again, the differences are none too great, and the individual and experimental variations are considerable.

(*f*) *Titration Values with Iodine Solutions*

The titration values of lignins with iodine solution when carried out according to the method of Walde and Hixon (7), also show a definite, but none too great, decrease with increasing degree of oxidation.

(*g*) *Acidmetric Titration Curves*

A comparison of the titration curves for unoxidized and moderately oxidized deciduous alkali lignins is shown in Fig. 1. In each case, 1 gm. of the moisture-

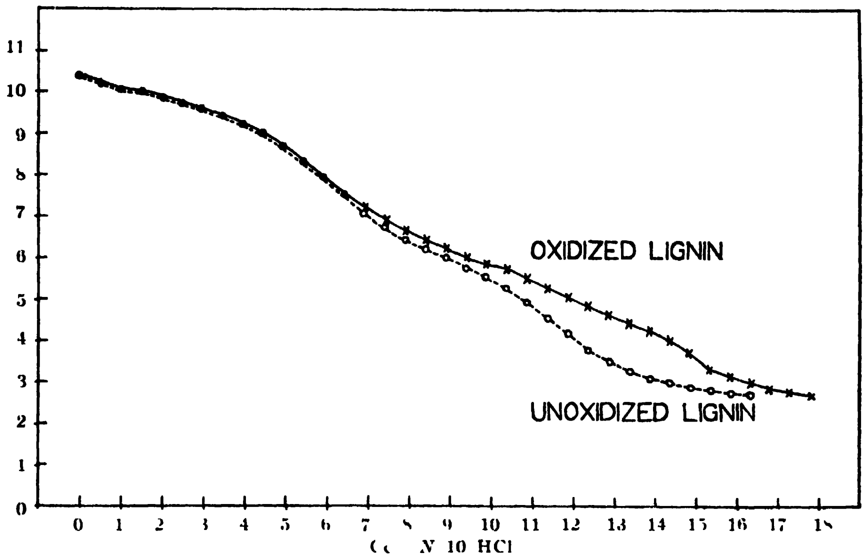

FIG. 1 *Titration curves.*

free lignin was dissolved in 1.34 cc. of $N/1$ sodium hydroxide, and the solution was diluted to 100 cc., and titrated with $N/10$ hydrochloric acid. The comparison of both curves shows the increased acidic nature of the oxidized lignin.

Unfortunately the inflection points are difficult to locate accurately. However, an approximation of the equivalent weight as based on the carboxyl group can be calculated and the following results are obtained:

	Unoxidized	Oxidized
Approx. pH 1st inflection point	8.0	8.0
" " 2nd " "	4.0	3.75
cc. $N/10$ HCl/gm. lignin	6.4	8.8
Approx. milliequivalent/100 gm.	64	88
Approx. equivalent weight, based on carboxyl group	1560	1135

(h) *Bicarbonate-neutralization Capacity of Lignins*

Another method of determining carboxyl groups is based upon base exchange, as worked out for cellulose by Wilson (8). This method was adapted for use in the analysis of lignin. The dried and finely ground weighed sample is suspended for two hours in dilute hydrochloric acid, filtered, washed until neutral, resuspended in 100 cc. of a solution containing $N/100$ sodium bicarbonate and $N/10$ sodium chloride, left in contact for one hour, then the lignin filtered off, and the solution back-titrated with dilute hydrochloric acid. From this, the "base-binding" ability of the lignin is calculated in milliequivalents per 100 gm. moisture-free lignin, as follows:

Carboxyl (as milliequivalents per 100 gm. lignin)

$$= \frac{100}{25G} \times \left(b - a - \frac{v.a}{100}\right),$$

where G = weight of m.f. lignin, in grams;
v = amount of moisture in lignin, in grams;
a = number of ml. of $N/100$ hydrochloric acid consumed by 25 ml. test solution at end of experiment;
b = number of ml. of $N/100$ hydrochloric acid consumed by 25 ml. sodium bicarbonate solution before start of experiment.

The above formula is calculated for the case where the lignin sample is suspended in 100 cc. of the sodium bicarbonate-sodium chloride solution, but where only 25 cc. of it is used in the back-titration.

An investigation of this method as applied to lignin indicated that equilibrium was approached at a very slow rate, so that the one hour test, as used by Wilson for cellulose, could not be used as an index of the actual carboxyl content.

In Table II are given data showing the effect of time and quantity of bicarbonate on the values obtained. Both dried and freshly precipitated samples of unoxidized and oxidized deciduous alkali lignins were used. It was observed that the immediate bicarbonate neutralizing capacity was considerably greater with the oxidized samples but that this differential was partially reduced after several days.

It should be borne in mind that neutralization values of 61 and 88 milliequivalents per 100 gm. for the oxidized and unoxidized lignins respectively were obtained by titration of aqueous solutions of the sodium salts. It is thus apparent that the bicarbonate neutralization test is influenced by not only the true carboxyl content but its accessibility in the solid phase, the rate of which is determined by the slow diffusion process.

It was noted that with the one hour test, values of the order of 4.0 milliequivalents per 100 gm. were obtained with unoxidized samples, as compared to values of around 20 to 22 for even mildly oxidized samples. The latter value

TABLE II

CARBOXYL DETERMINATIONS ON LIGNINS UNDER VARYING CONDITIONS

Type of lignin	Unoxidized			Oxidized		
	2.5 gm. of lignin susp. in $NaHCO_3$ NaCl		Carboxyl, milli-equiv. /100* gm.	2.5 gm. of lignin susp. in $NaHCO_3$ NaCl		Carboxyl, milli-equiv. /100* gm.
	Quantity, cc.	Time, hr.		Quantity, cc.	Time, hr.	
Dry	100	1	4.05	100	1	22.57
	"	4	9.00	"	4	24.92
	"	16	14.22	"	16	28.68
	"	22	14.62	"	22	30.17
	"	46	20.82	"	46	31.30
	500	1	4.00	500	1	28.15
	"	4	9.29	"	4	29.88
	"	16	18.07	"	16	33.70
	"	22	20.31	"	22	36.30
	"	46	25.07	"	46	41.79
Wet (freshly precipitated)	100	1	8.86	100	1	18.93**
	"	16	17.59	"	22	21.46**
	500	1	7.27	500	1	31.70**
	"	22	19.91	"	22	20.96**

*See also Table V.
**Samples difficult to filter, thus impairing reproducibility of results.

did not increase with increasing oxidation, as did the lyophilic properties, as will be later shown in Table V. Such a test may prove useful for distinguishing between so-called unoxidized lignins for use in plastics, and other lignins that have received more or less oxidation treatment.

(*i*) *Ion Exchange Experiments*

Similar conclusions with regard to the accessibility and increased acidity of the oxidized lignin can be drawn from ion exchange experiments. Weighed crystals of calcite were added to aqueous 10% suspensions of unoxidized and moderately oxidized deciduous alkali lignins, which were kept in a constant temperature bath at 25° C. At intervals these crystals were taken out, washed, dried, weighed, and returned to the lignin suspensions.

As seen in Fig. 2, the calcite crystals in contact with the suspension of the oxidized lignin lost weight much faster than the ones left with the unoxidized lignin, or, in other words, oxidized lignin is a better ion exchanger than unoxidized lignin. This observation has already been made by Bennett (1), who drew from it his conclusions as to the mechanism of humus formation in the soil.

The above reported ion exchange experiment was interrupted after 199 days and the lignins were filtered off and analyzed. A comparison of the lignin characteristics at the start of the experiment and after 199 days is given in Table III.

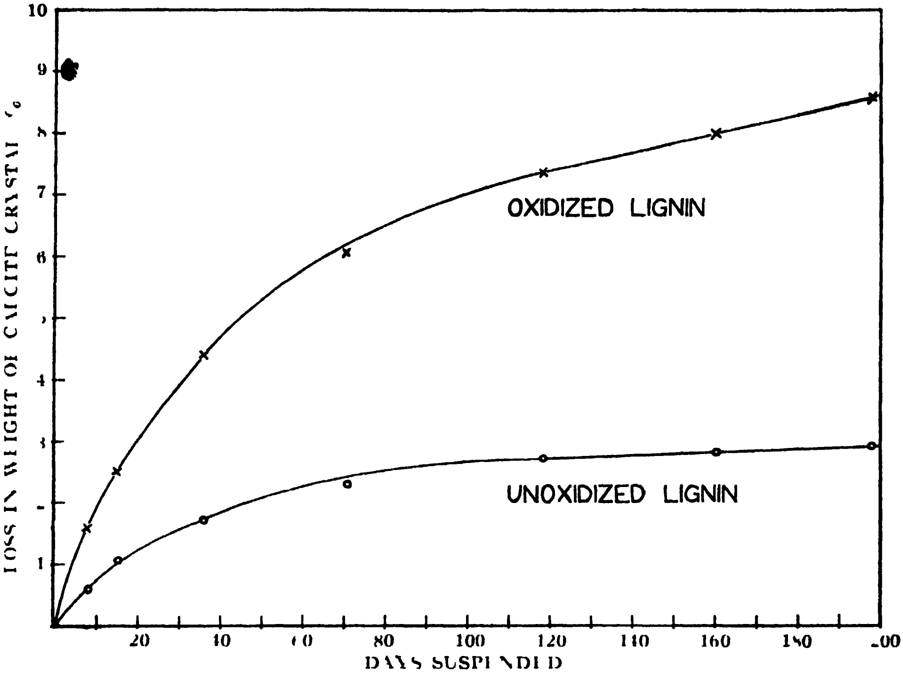

FIG. 2. *Ion exchange tests.*

TABLE III

ION EXCHANGE TESTS
(Averages from triplicates)

Type of lignin used	At start of experiment: % ash anal.	Melting points, °C: Open tube method, Shrink	Open tube method, Melt	Mercury covered tube method, Shrink	Mercury covered tube method, Black	Mercury covered tube method, Gas	Electric stage	pH of susp.
Unoxidized	0.33	160	170	157	161	168	157	6.28
Oxidized	0.53	215	228	186	216	223	213	5.94

Type of lignin used	After contact with calcite crystals for 199 days at 25° C.: % Ash, Anal.	% Ash, Calcd. from loss in wt. of crystals*	Melting points, °C: Open tube method, Shrink	Open tube method, Melt	Mercury covered tube method, Shrink	Mercury covered tube method, Black	Mercury covered tube method, Gas	Electric stage	pH of susp.
Unoxidized	1.01	1.20	175	183	168	172	175	171	6.70
Oxidized	2.21	2.48	None	Above 250	265	295	304	Above 300	6.31

**The amounts of ash found in the samples at the start of the experiment were added to the amounts of ash to be expected from the loss in weight of the suspended calcite crystals.*

Both the melting point and the ash content of the lignins showed increased values after treatment with the calcite crystals, the oxidized lignin showing the greatest changes. The increases in ash content are proportional to the losses in weight of the suspended calcite crystals. The suspensions of the oxidized samples at the start as well as at the end of the experiment show a lower pH than do those of the unoxidized samples.

Volumetric Measurements of the Lignin-Oxidation Reaction

(*a*) *Equipment and Procedure*

A closer study of the oxidation reaction of lignin necessitated a more exact technique than that used when lignin batches are oxidized in the preparation of lignin-rubber coprecipitates for compounding, curing, and testing.

The equipment in which these experiments were carried out is shown in Fig. 3. An amount of air-dry lignin, corresponding to 2.63 gm. moisture-free

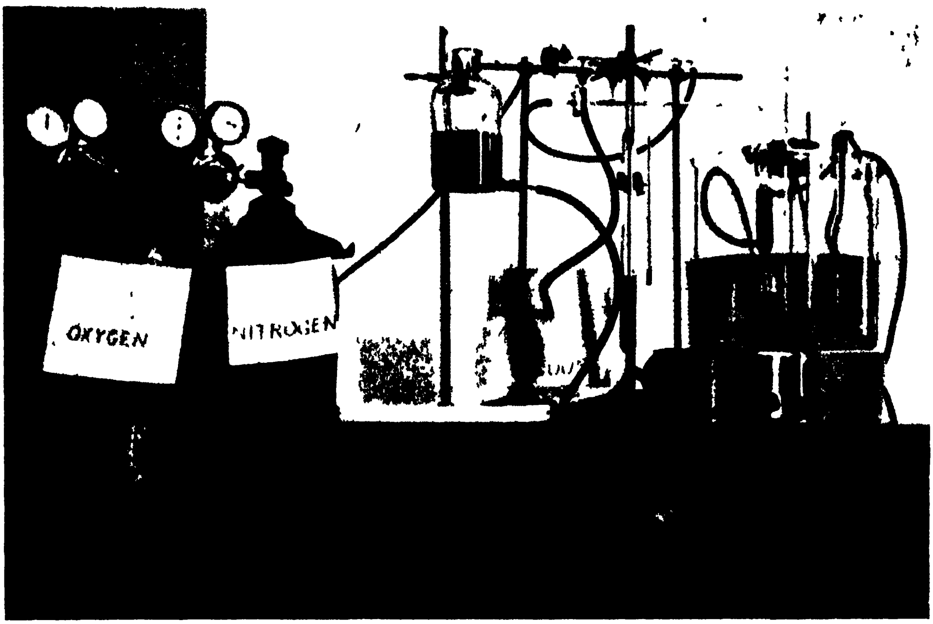

FIG. 3. *Apparatus used for volumetric determination of oxygen absorption*

weight, was placed in a glass bulb, 3 in. high and $1\frac{1}{2}$ in. wide. To this was added 13.15 gm. of a solution of sodium hydroxide, containing 20 gm. sodium hydroxide in 1000 cc. This yielded a solution containing 10% lignin and 1% sodium hydroxide, with an initial pH of approximately 11. A small magnetized stirring bar was introduced, which allowed the solution to be stirred magnetically from outside. The bulb was inserted in a constant temperature bath and connected with one arm of a gas burette. The other arm of the gas burette led to a mercury gauge and from there to a manifold, the four

outlets of which were connected with the open air, the vacuum pump, a nitrogen cylinder, and an oxygen cylinder, respectively. The liquid used as a seal was a concentrated solution of sodium chloride.

The experiment was started by repeatedly evacuating the whole apparatus and refilling it with nitrogen. Then the bath was brought up to the reaction temperature, in most cases 70° C., and the lignin sample kept under nitrogen until constancy of the volume, as read on the gas burette, indicated that constant temperature conditions had been established and that no leakage occurred. The apparatus was then repeatedly evacuated and refilled with oxygen. The vessel containing the sealing liquid was then adjusted to such a height that the distance between the surface of the liquid and the meniscus in the gas burette was 8 in., this distance being kept constant during the run. The surface of the sealing liquid and the meniscus in the gas burette were then brought to equal level, the first reading on the gas burette was taken, and the time counted from there on. This and later volume readings were converted to 0° C., and 76 cm. pressure, and the volume changes converted into grams of oxygen. The results were evaluated by relating the number of grams of consumed oxygen to the weight of the lignin sample, and reported in grams of oxygen absorbed by 100 gm. of lignin, i.e., as % oxygen absorbed.

It has already been mentioned that lignin solutions, while being oxidized, undergo a drop in pH. Basically, two ways of oxidizing lignin solutions can be visualized. Either the pH of the lignin solution is allowed to drop during oxidation, or such a drop is prevented by continually adding caustic while oxidizing. The latter method was used when preparing the oxidized lignins described in Table V, since it was found that a drop in pH causes the oxidation to gradually slow up to an extent that was found to be impractical.

However, in some of the volumetric oxidations discussed here, the pH was allowed to drop. Volume readings were taken at various intervals and converted as previously described.

In other of the volumetric experiments, where the pH was kept at its original value of about 11 during the whole experiment, the apparatus was repeatedly evacuated and refilled with nitrogen after each two hours of running with oxygen. After the oxygen had been replaced by nitrogen, the reaction vessel was opened, a predetermined amount of sodium hydroxide solution was added, and the reaction vessel again connected with the gas burette, repeatedly evacuated, and refilled with oxygen. A new volume reading was taken and the reaction allowed to proceed undisturbed for another two hours, after which time the procedure was repeated. The amount of sodium hydroxide to be added each time had to be determined in separate experiments, since the described setup did not allow a direct pH observation.

Each of these oxidations was carried on for a certain number of hours. The oxidation was then stopped by replacing the oxygen by nitrogen, and again making certain of absence of any leakage by observing the stability of the meniscus of the gas burette over a period of one to two hours.

The contents of the reaction bulb was then diluted and the pH measured. In those series in which the pH had been maintained during the run by continuous addition of sodium hydroxide, the pH at the end of each fairly long run was found to be close to the original value of 11. The lignin solution was then acidified to a pH of approximately 2.5, heated to 90° C., filtered, and the washed lignin dried in the open air and then for 30 min. at 105° C. With these samples, melting point determinations were carried out, and after redissolving in sodium hydroxide and mixing with rubber latex, lignin-containing rubber crumbs were coprecipitated.

(*b*) *Oxidation Rates at 70° C.*

In experiments with deciduous alkali lignin, in which the pH was allowed to drift during oxidation, results as shown in Fig. 4 were obtained. Oxygen

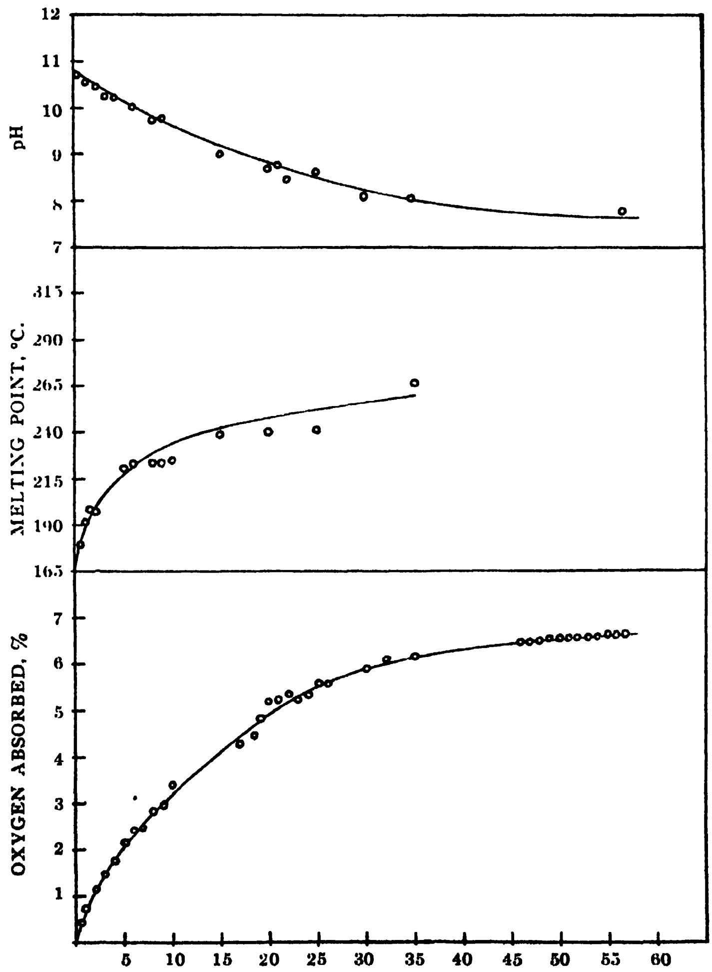

FIG. 4. *Oxidation at 70° C.—pH drift.*

is absorbed at a fairly constant rate for the first 20 hr. This absorption is accompanied by a drop of pH from its initial value of 10.8 to approximately 9, and an increase occurs in the melting point of the lignin to approximately 245° C., as determined by the open-tube method. Owing to the lower pH, the oxidation then slows up considerably, and so does the rate of decrease in pH.

The progress of the reaction is quite different if the pH of the lignin solution is kept at its original value of around 11 during the whole oxidation by regular additions of small amounts of sodium hydroxide. As Fig. 5 shows, the rate

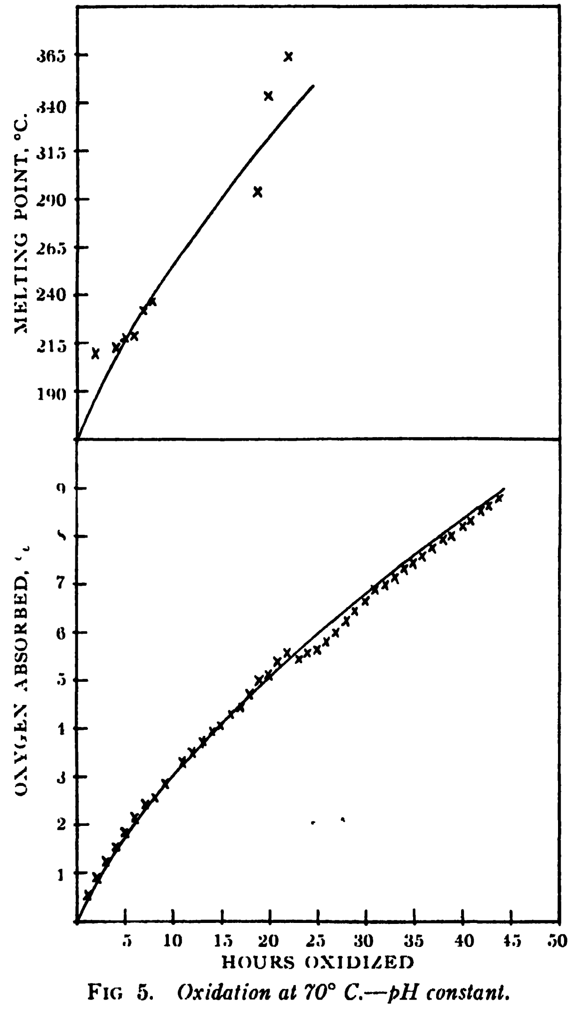

FIG. 5. *Oxidation at 70° C.—pH constant.*

of oxygen absorption is fairly constant over the investigated range, with only slight signs of slowing up as the absorption progresses. The melting point curve follows the same pattern, and lignins with high melting points are obtained at a fairly early stage of the oxidation.

By plotting the melting points and the pH values against the percentage of absorbed oxygen for both series together in one graph, Fig. 6 is obtained. This figure reveals the rather surprising effect that the same percentage of absorbed oxygen raises the melting point of the oxidized lignin considerably higher when the pH was kept constant during the oxidation than when it was allowed to drop.

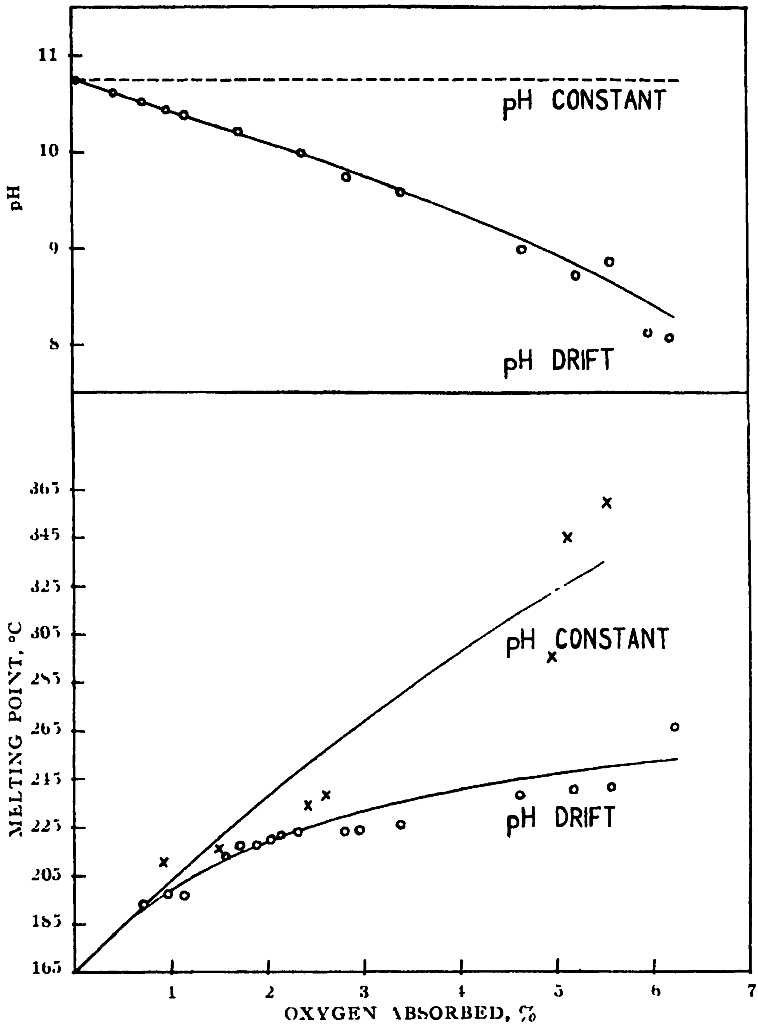

FIG. 6. *Oxidation rate vs. pH.*

In other words, higher pH in the lignin solution not only increases the speed of the oxidation, which results in a higher absorption of oxygen after a certain length of time, but it also yields lignins of higher melting points for the same amount of oxygen absorbed. Thus, the mechanism of lignin oxidation seems to depend on the pH of the lignin solution.

Whether or not lignins of the same melting point, but oxidized at different pH values, differ could not be established, but there is no indication that this is the case. GR–S-containing crumbs, prepared from either lignin under otherwise identical conditions, have the same appearance.

As shown in Figs. 5 and 6, experiments in which the pH was kept constant showed only a slight decrease in the rate of oxygen consumption, even after longer exposure. This would suggest that oxidized lignins, when subjected to further oxidation, could not be expected to show too great a reduction in the rate of oxygen absorption, when compared with lesser or even unoxidized lignin samples. Thus, the possibility of distinguishing between lignins of various degrees of oxidation by this volumetric oxidation method seemed rather slight.

Nevertheless, experiments were carried out to compare the oxygen absorption by unoxidized and oxidized deciduous, as well as coniferous alkali lignins, the pH being allowed to drift. The results are plotted in Fig. 7. The lignin characteristics at the start of the runs and after 20 hr. oxidation are given in Table IV.

As indicated by Fig. 7, both unoxidized deciduous and coniferous alkali lignins absorb oxygen at approximately the same rate, with the same final pH. The oxidized lignins, as was to be expected, took up oxygen somewhat more slowly than the unoxidized samples, but without showing sufficient difference to distinguish lignins of varying degree of oxidation.

TABLE IV

Type of lignin used	Melting point at start, ° C	After 20 hr.	
		Melting point, °C	% oxygen absorbed
Unoxidized deciduous alkali	168	245	4.9
Oxidized deciduous alkali	349	Not at 360	3.6
Unoxidized coniferous alkali	208	Not at 360	5.0
Oxidized coniferous alkali	Not at 360	Not at 360	3.9

NOTE: *The above reported melting points were determined by the open-tube method*

What apparently happens is that treatment of lignin with oxygen, on the alkaline side, first opens up new acidic groupings in the lignin molecule, but soon starts degrading the molecule more and more, forming low molecular, acidic degradation products, and causing the remaining lignin to assume increasingly lyophilic properties, and eventually completely degrading the remaining lignin skeleton.

Fig. 7 also shows that unoxidized deciduous alkali lignin, when suspended in water and treated with oxygen at 70° C., undergoes only comparatively little oxidation, with an increase in melting point after 20 hr. from 169° C. to only 180° C., and correspondingly low oxygen consumption.

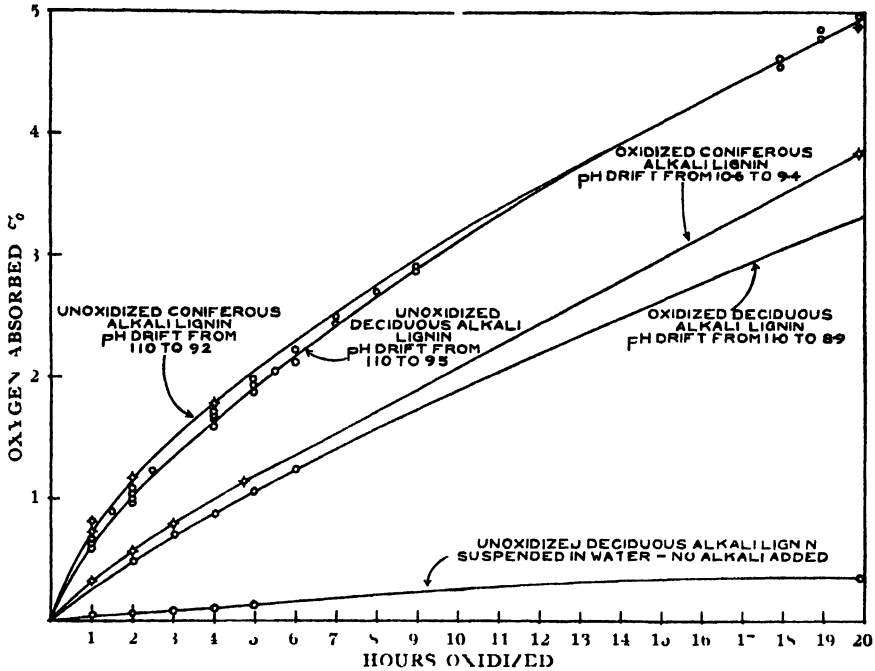

FIG 7 *Oxidation rates for various lignins at 70° C —pH drift*

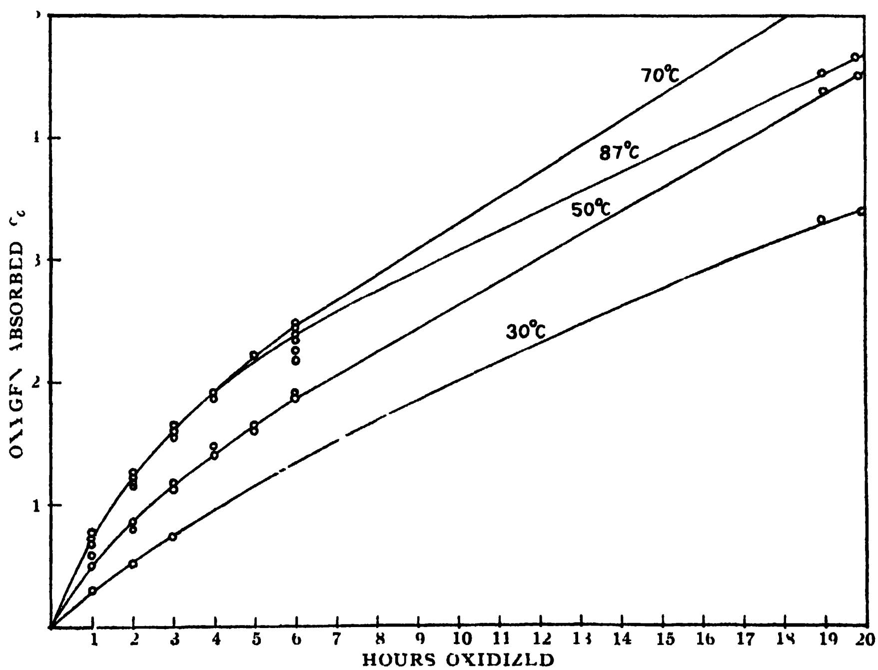

FIG 8 *Oxidation rates at various temperatures—pH drift*

A sample of dry unoxidized deciduous alkali lignin, when subjected to oxygen at 70° C. for 20 hr., showed no measurable oxygen consumption, with an increase in melting point to only 177° C.

(c) *Oxidation Rates at Temperatures Below and Above 70° C*

It seemed also to be of interest to investigate the rates of oxidation for the same lignin, under otherwise identical conditions, at various temperatures.

Results of experiments of this kind are shown in Fig. 8. At temperatures below as well as above 70° C., the rate of oxidation seems to slow down.

TABLE

SUMMARY OF

Deciduous alkali lignin type	Oxidation conditions: Equipment	Hours	Temp. °C	pH	Filter tests on precip. lignin[1]: Filter time, sec.	Water in cake, % on lignin	Appearance of dried cake	Melting points of lignin, °C: Open tube method: Shrink	Melt	Mercury-covered tube method: Shrink	Black	Gas	Electric stage
Pure	Not oxidized				72	302	brown powdery	161	178	150	152	162	165
Pure	Roto-Clone	[illegible]	[illegible]6	10.[illegible]1	123	374		181	196	176	180	179	180
Pure	Tower	20	81	10.40	280	44[illegible]		20[illegible]	214	191	193	218	201
Crude	Tower	33	70	10.75	375	431		207	217	182	200	217	205
Crude	Tower	20	70	10.75	[illegible]	438	Continual change	216	224	191	211	220	212
Crude	Tower	20	70	10.85	158	421		211	228	177	210	221	213
Pure	Roto-Clone	[illegible]	66	10.39	213	419		212	257	197	200	233	217
Pure	Roto-Clone	8	66	10.49	118	44[illegible]	Black horny	none	289	none	241	[illegible]0[illegible]	238
Crude	Drum		70	10.10	317	536		none	[illegible]	none	226	268	226

[1] *A 10% solution of the lignin containing 51 gm. of lignin and 5.1 gm. sodium hydroxide was precipitated at 90° C. to a pH of 2.5. Washing with 5[illegible] cc. of water at 90° C.*
[2] *Derived from Fig. 6 using the 'open tube' method melting points.*
[3] *Exactly 2.5 gm. dry lignin suspended in 100 cc. of N/100 sodium bicarbonate + N/10 sodium chloride for one hour and loss in alkalinity of the solution determined.*

The decrease caused by the lowering of the reaction temperature is obviously due to the ordinarily observed temperature trend of exothermic reactions, whereas the decrease at temperatures above 70° C. can probably be attributed to the decreased solubility of the oxygen in the lignin solution.

Conclusions

Although the oxidation range that has been studied is rather small, yield determinations indicate that even in this narrow range considerable amounts of lignin, up to 20%, are degraded to products of acidic character, of sufficiently low molecular weight to evade precipitation by subsequent acidification. This

suggests that more intense oxidation would probably break down the whole of the lignin molecule, as already observed by others, whereas mild oxidation causes primarily the formation of carboxyl groupings, without considerably changing the internal structure of the molecule, as already suggested by Freudenberg. The melting point of the lignin and its lyophilic properties are increased by continued oxidation, and, as already pointed out, these two properties seem to be mainly connected with and possibly responsible for the reinforcing properties in rubber.

A survey of all the data obtained on deciduous alkali lignins of varying

V

TEST RESULTS

Lignin characteristics						Filter tests on wet precip lignin GR-S crumb			Test results on batch oxidized lignins Coprecipitate with GR-S compounded and cured [6]					
% [2] Oxygen taken up by oxidat	% CuO deposit from Fehling soln	% Iodine consum	Carboxyl [3] milli equiv 100	% Methoxyl	[4] Viscos	Filter time sec	Water in cake % on solids	[5] Filtering considered	Best cure	Tensile, psi	Elong %	Modulus 300%	C P Mooney	Overall reinforc
None	12.05	315	6.48	19.70	4.24	20	74	Good	20	1810	790	411	60	Poor
1.0%	7.55		23.42	19.60	4.58			Good	60	2678	700	677	78	
1.3%	7.32	301	23.29			22	162	Excel	60	3119	650	900*	84	Good
1.5%						16	141	Very good	60	3220	680	1005		
1.6%						13	128	Very good	65	3100	650	1090		
1.8%					4.70	15	138	Very good	60	3185	680	1005		
2.0%	4.91		21.22	19.30		21	153	Fair	10	2521	700	700	74	
3.5%	5.52	291	25.48			35	221	Poor	50	2719	730	717	86	Satisfactory
5.3%	6.70		18.10	18.90		42	216	Very poor	70	2521	750	649		

[4] Measured on a 10% solution in cellosolve.
[5] Crumb containing 17 gm lignin + 34 gm GR-S coprecipitated at 90° C.
[6] All lignin-GR-S crumbs were prepared by coprecipitation of mixtures of 10% lignin solution plus 30% GR-S-latex, in the ratio of lignin to GR-S solids 1 to 2 at 90° C by acid and brine.
[7] Strength tests carried out by Research Department of Polymer Corporation Limited, in Sarnia, published with their permission.

degrees of oxidation as well as of their coprecipitates with GR-S latex is given in Table V. The lignins discussed therein are arranged by starting with unoxidized lignin ("Tomlinite") and progressing through medium-oxidized towards overoxidized samples, as indicated by the increase in melting point. The filter tests on the precipitated lignins show the increase in their lyophilic properties resulting from increasing degree of oxidation, as indicated by slower filtering rate and a higher percentage of water content in the filter cake. The appearance of the dried cake also changes gradually, the cake being brown and powdery in the unoxidized lignins, and turning gradually black and horny in the "overoxidized" samples.

Also reported in Table V are the melting points obtained by the three methods, whose interrelation has already been discussed. The technique of oxidation used in the preparation of the lignins described in Table V did not allow a quantitative measurement of the oxygen consumed.

However, volumetric experiments as outlined in the previous section have allowed an estimate of the amount of oxygen taken up by lignin for any given melting point. Thus the appropriate values obtained in this way have been included in Table V under the heading "% Oxygen Taken Up by Oxidation". It appears that an absorption of 1.3 to 2.0% oxygen by the regular "Tomlinite" yields a lignin best suited as a reinforcing agent for GR-S, if coprecipitation is carried out between 80° and 90° C., and if the solutions are not too dilute.

Also shown in Table V are other lignin characteristics, such as copper number, iodine value, carboxyl number, methoxyl content, and viscosity in cellosolve, the significance of which has already been discussed.

The wet crumbs which were coprecipitated in a ratio of 2:1 at 80° to 90° C. from mixtures of 30% latex with 10% lignins of varying degrees of oxidation behave similarly to the corresponding lignins if coprecipitated under identical conditions in so far as filter times and moisture contents are concerned. In general the higher the degree of oxidation, the slower is the filtering rate and the higher is the water content in the wet crumb.

These lignin-containing crumbs were dried, compounded, cured, and tested in the manner previously described (5). The results obtained are shown in Table V and, assuming identical coprecipitation conditions, indicate poor reinforcement by unoxidized and very slightly oxidized lignins and good reinforcement by medium oxidized lignins. The reinforcement again becomes poorer for "overoxidized" samples, which are also harder to handle in milling and compounding.

Acknowledgment

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RATION BISCUITS

V. EFFECTS OF KIND AND CONCENTRATION OF VARIOUS CONSTITUENTS ON KEEPING QUALITY[1]

By H. J. Lips[2], J. B. Marshall[3], W. Harold White[4], and G. A. Grant[5]

Abstract

Ration-type biscuits commercially prepared according to a basic formula, with increasing levels of supplementary ingredients tested one at a time, gave the following results for flavor tests and chemical analyses when stored in sealed cans at 110° F. for periods up to 88 weeks: flavor score was improved by sugar and impaired by skim milk powder and salt; peroxide oxygen value of extracted fat was increased by salt and decreased by defatted soybean flour; fluorescence of a potassium chloride extract of defatted biscuit was increased by defatted soybean flour, baking soda, skim milk powder, malt, and salt, and decreased by sugar; pH of the potassium chloride extract was increased by defatted soybean flour and soda, and decreased by skim milk powder and malt. Shortening stability was a limiting factor in determining the relative effects of the other components on biscuit keeping quality. Biscuits containing all the supplementary materials had good keeping quality when a stable vegetable shortening was used.

Introduction

Previous papers on simple formula ration biscuits from these laboratories described effects of shortening, moisture, and a number of protein supplements on keeping quality (4, 6, 8, 11). However, the stability of ration biscuits might be influenced by the kind and concentration of any constituent, and by various interactions between added materials. Other work has indicated the stabilizing action of molasses and spices (9), sugar (3, 7) and wheat oil (12) in crackers, and the deleterious action of salt in processed cereal flakes (13). This paper describes experiments to determine the effect of some of the more commonly used ingredients, singly and in combination, on the keeping quality of stored biscuit material.

Materials and Methods

Four series of biscuits were commercially prepared according to a basic formula, with extra materials added in concentrations expressed as percentages of the amount of soft wheat flour in the basic formula. Two types of shortening, animal-vegetable and hydrogenated all-vegetable, were used. The basic formula was 50 lb. soft wheat flour, 5 lb. shortening, 6 oz. baking soda, and water as required.

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[2] *Biochemist, Fats and Oils Laboratory.*

[3] *Biologist, Food Investigations.*

[4] *Formerly Biochemist, Food Investigations, now Chemist, Imperial Oil Co., Ltd., Sarnia.*

[5] *Formerly Technical Officer, Food Investigations, now Technical Officer, Defence Research Laboratories, Ottawa.*

In Series I (animal–vegetable shortening No 1) whole wheat flour and defatted soybean flour were each tested in three concentrations as *substitutes* for part of the soft wheat flour, and baking soda was tried at five levels (Table I) In Series II (hydrogenated vegetable shortening No 1) skim milk powder, malt, salt, and sugar were tested as *additions* to the basic formula in the varying concentrations shown in Table II, and the amount of shortening adjusted slightly when necessary to give a satisfactory mix The same materials used in Series I and II were used in Series III (animal–vegetable shortening No 2), at single concentrations only (the median values of the concentration ranges in the first two series), in order to determine the relative effects of the different supplements (Table III)

As it would have been laborious to determine the results of simultaneous variation of a large number of constituents at several concentrations of each, Series IV (hydrogenated vegetable shortening No 2) was designed to test the effect of *omitting*, one at a time, whole wheat flour, defatted soybean flour, skim milk powder, malt, salt, and sugar from a complete formula (Table IV) Whole wheat flour (40%) was *substituted for part of* the soft wheat flour in the basic formula, and soybean flour (20%), skim milk powder (20%), malt (6%), salt (2 25%), and sugar (20%) were *added to* the basic formula It was necessary to adjust these amounts slightly as each supplementary constituent was omitted in turn, but the total of soft wheat and whole wheat flour was maintained at 50 lb in each of the batches The quantity of shortening was increased from 5 lb to 8 lb

Preliminary determinations of fat and moisture (4) and of nitrogen (1) showed that the desired proportions had been satisfactorily approximated in all the preparations Moisture contents were all between 6 and 9%, a range unlikely to cause stability differences (8) The biscuits were stored in sealed No 1 cans at 110° F, and sampled at eight-week intervals for periods up to 88 weeks Deterioration was assessed by peroxide oxygen, pH, and fluorescence determinations, and by flavor scores, according to methods previously described (4, 8) The results of Series I and II were examined by fitting regression lines to the data for each variable, and by analyses of variance

Results

For all series of biscuits, the flavor scores and peroxide oxygen values obtained at different storage times were rather irregular, whereas pH and fluorescence measurements were more consistent Peroxide values tended to fall after reaching a maximum, while fluorescence values tended to level off after an early rise In general, however, peroxide oxygen and fluorescence values rose and pH values fell as the flavor of the biscuit materials deteriorated, but the magnitude and speed of these changes varied considerably with the kind and concentration of the supplementary ingredients Graphical pre-

sentations of similar changes in biscuit material were made in earlier papers (4, 6, 8, 11). Mean values over all samplings for the different measurements are shown in Tables I to IV.

Biscuits of Series I and III (animal–vegetable shortenings) remained acceptable for 16 to 40 weeks, and those of Series II and IV (hydrogenated vegetable shortenings) remained acceptable for 72 to 88+ weeks.

Series I and II

To determine the effect of increasing the amount of each of the different materials tested, irrespective of storage time, the data for each group of

TABLE I

MEAN VALUES OVER ALL SAMPLINGS FOR 24 WEEKS FOR KEEPING QUALITY MEASUREMENTS ON BISCUITS STORED AT 110° F

(Series I, animal vegetable shortening No 1)

Supplementary ingredient, %		Flavor score, 0-10 basis	Peroxide value, ml of 0 002 N thiosulphate per gm of extracted fat	pH of potassium chloride extract of defatted biscuit	Fluorescence of potassium chloride extract of defatted biscuit, Coleman photofluorometer units
Whole wheat flour	10	7 6	3	6 8	39
	25	7 6	2	6 9	37
	40	7 4	4	6 7	38
Defatted soybean flour	4	7 1	12	6 8	44
	12	7 3	8	7 0	18
	20	7 3	5	7 0	51
Baking soda*	0 25	6 0	82	6 5	23
	0 50	6 2	94	6 5	36
	0 75	6 1	18	6 8	12
	1 00	6 1	76	6 8	43
	1 25	6 1	39	7 7	48

* *These values represent total amounts of soda in the biscuit*

constituents were first examined separately. Only three components gave siginficant regression coefficients for flavor change with change in concentration (Table V). Increasing the amount of skim milk powder or salt was detrimental to flavor score, while additional sugar tended slightly to improve it. Additional amounts of soda tended to depress flavor at 8 and 16 weeks' storage and to increase it at 24 weeks, but showed no effect at the other sampling periods. Whole wheat flour, defatted soybean flour, and malt had no demonstrable concentration effect on flavor

On the average, peroxide oxygen value decreased with additional amounts of soybean flour, and increased with additional amounts of salt, but was insensitive to changes in quantity of the other ingredients.

TABLE II

MEAN VALUES OVER ALL SAMPLINGS FOR 88 WEEKS FOR KEEPING QUALITY MEASUREMENTS ON BISCUITS STORED AT 110° F

(Series II, hydrogenated vegetable shortening No 1)

Supplementary ingredient, %		Flavor score, 0-10 basis	Peroxide value, ml of 0.002 N thiosulphate per gm of extracted fat	pH of potassium chloride extract of defatted biscuit	Fluorescence of potassium chloride extract of defatted biscuit, Coleman photofluorometer units
Skim milk powder	4	6.1	2	6.1	20
	12	5.6	2	6.0	33
	20	5.2	2	6.0	43
Malt	2	6.8	2	5.9	27
	4	6.8	2	5.7	32
	6	6.9	2	5.7	39
Salt	0.75	6.9	3	5.8	20
	1.50	6.6	3	5.8	19
	2.25	6.6	5	5.8	24
Sugar	4	7.4	2	5.9	17
	12	7.5	1	6.0	13
	20	7.6	2	5.8	13

pH tended to diminish with additional skim milk powder and malt, and to increase with additional soda (as expected) and soybean flour It was unaffected by variation in amounts of whole wheat flour, salt, and sugar

Fluorescence was increased in varying degree by the incorporation of additional amounts of soybean flour, soda, skim milk powder, malt, and salt, but was reduced by added sugar Varying the amount of whole wheat flour produced no significant change

TABLE III

MEAN VALUES OVER ALL SAMPLINGS FOR 24 WEEKS FOR KEEPING QUALITY MEASUREMENTS ON BISCUITS STORED AT 110° F

(Series III, animal-vegetable shortening No 2)

Supplementary ingredient, %		Flavor score 0-10 basis	Peroxide value ml of 0.002 N thiosulphate per gm of extracted fat	pH of potassium chloride extract of defatted biscuit	Fluorescence of potassium chloride extract of defatted biscuit, Coleman photofluorometer units
Whole wheat flour	25	6.8	11	6.4	48
Defatted soybean flour	12	6.6	8	6.8	41
Baking soda	0.75*	6.5	4	6.8	29
Skim milk powder	12	6.9	2	6.6	41
Malt	4	6.6	2	6.5	52
Salt	1.5	6.2	14	6.5	27
Sugar	12	6.5	14	6.8	25

*This value represents the total amount of soda in the biscuit

TABLE IV

MEAN VALUES OVER ALL SAMPLINGS FOR 88 WEEKS FOR KEEPING QUALITY MEASUREMENTS ON BISCUITS STORED AT 110° F.

(Series IV, hydrogenated vegetable shortening No. 2)

Supplementary ingredient *omitted* from complete formula	Flavor score, 0-10 basis	Peroxide value, ml of 0.002 *N* thiosulphate per gm of extracted fat	pH of potassium chloride extract of defatted biscuit	Fluorescence of potassium chloride extract of defatted biscuit, Coleman photofluorometer units
None (complete)	6 4	2	5 9	91
Whole wheat flour	6 5	2	6 1	77
Defatted soybean flour	7 1	2	6 3	52
Skim milk powder	7 0	4	6 5	41
Malt	6 4	2	6 1	62
Salt	6 7	2	6 0	85
Sugar	6 2	2	5 9	89

For those constituents showing no effects related to concentration, the question remained whether they nevertheless modified the characteristics of all biscuits in which they were present, regardless of amount. Suitable comparisons could be made only among biscuit groups prepared with the same shortening. Analyses of variance of the comparative flavor scores for whole wheat and soybean flour biscuits demonstrated a more rapid deterioration of

TABLE V

AVERAGE CHANGES IN MEASUREMENTS OF KEEPING QUALITY OF BISCUITS STORED AT 110 °F FOR EACH PER CENT INCREASE IN CONSTITUENT CONCENTRATION

(Series I and II)

Keeping quality measurement	Constituent	Regression coefficients,* representing change in keeping quality measurements for each per cent increase in constituent concentration
Flavor score, 0-10 basis	Skim milk powder	06
	Salt	− 21
	Sugar	01
Peroxide oxygen value, ml of 0 002 *N* thiosulphate per gm of extracted fat	Defatted soybean flour	− 42
	Salt	2 33
pH of potassium chloride extract of defatted biscuit**	Defatted soybean flour	.02
	Baking soda	86
	Skim milk powder	− 01
	Malt	− 02
Fluorescence of potassium chloride extract of defatted biscuit, Coleman photofluorometer units	Defatted soybean flour	44
	Baking soda	19.53
	Skim milk powder	1 41
	Malt	3 06
	Salt	2 61
	Sugar	− 26

**Only statistically significant coefficients (5% level) presented.*

***As pH values are logarithmic, changes of the same numerical magnitude in different pH ranges are not equivalent.*

the latter during storage. Peroxide oxygen value was higher at the earlier sampling times in the sodium bicarbonate biscuits than in those containing whole wheat flour; it was significantly lower at 40 to 56 weeks in biscuits containing sugar than in those having skim milk powder or malt; but these differences were not evident at other sampling times for the same materials. Biscuits containing salt or sugar did not differ in pH changes.

Series III

Measurements for Series III biscuits (animal-vegetable shortening), shown in Table III, indicated a somewhat different relative effect of supplementary constituents than did the measurements for the corresponding batches of Series I and Series II biscuits. Whole wheat flour and defatted soybean flour biscuits were only slightly superior to the soda batch in flavor, and had higher peroxide and fluorescence values. In the presence of the animal-vegetable shortening, sugar appeared to have little effect either in improving flavor or preventing formation of peroxides in the fat fraction. Skim milk powder appeared to have a stabilizing effect, as opposed to its undesirable action in Series II with the more stable (vegetable) shortening. However, the action of salt was deleterious, as before.

Series IV

The results for the series in which individual constituents were omitted, one at a time, from a complete formula (Table IV) showed that these samples differed very little in keeping quality, all remaining acceptable for 80 to 88 weeks at the storage temperature of 110° F. The sample without skim milk powder appeared to differ most widely from all others in the group, having relatively good flavor, high pH, and low fluorescence but high peroxide value. The omission of defatted soybean flour also appeared to improve the flavor of the biscuit material.

Discussion

A variety of effects due to variations in constituents is possible in biscuits, and some of those described have apparently not been reported heretofore. The improvement of flavor with increasing amounts of sugar could be expected, since sugar at high concentrations functions as an antioxidant for fats (3, 7) and its taste can serve to mask unpleasant flavors. Soda may improve flavor and maintain a desirable pH by neutralizing acidic products of fat deterioration, but an excess imparts a characteristic, unpleasant taste. The use of higher alkali concentrations also causes more gasification, which allows coloring and scorching to take place more easily during baking, and scorching leads to a decrease in keeping quality (12). The sugars in malt and skim milk powder should function as stabilizers, but the action of the malt and milk powder is no doubt complicated by their content of protein and other materials. The action of salt in accelerating rancidity may be due to the presence of other chlorides as impurities (5). Whole wheat flour should function as a better stabilizer than soft wheat flour because of its greater

content of natural antioxidant material. This is in line with the observation that the addition of starch to soften a flour gives poorer biscuit keeping quality (9). Full-fat soybean flour is said to be an effective antioxidant, but this property may be diminished when the flour is defatted (10). However, flour prepared from extracted soybean meal stabilized both dry pastry mixes and baked pastry (2).

It should be noted that the poor stability of the shortening used in the whole wheat flour, soybean flour, and soda groups of Series I may have influenced the results obtained with varying concentrations of these materials. The *relative* effects of different added materials also appeared to depend on the type of shortening used. For example, skim milk powder, which improved biscuits prepared with animal vegetable shortening, appeared to have the opposite effect in the presence of the more stable hydrogenated vegetable shortening. The data support earlier evidence (6) that shortening stability is a limiting factor in biscuit storage life and suggest that biscuits of good keeping quality can be prepared containing any of the supplementary materials described, if a stable vegetable shortening is used.

The observed variation in the objective measurements with nature and concentration of the supplementary ingredients emphasizes the importance of supporting these objective estimates of quality with palatability tests.

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THE ADSORPTION OF SODIUM MYRISTATE BY CARBON BLACK[1]

BY MARGUERITE A. READE,[2] A. S. WEATHERBURN,[2] AND C. H. BAYLEY[2]

Abstract

The adsorption of sodium myristate from 0.1% aqueous solution by a series of carbon blacks and an activated charcoal has been measured at 70° C. In every case a preferential adsorption of fatty acid was observed. The extent of adsorption of both the fatty acid and alkali components of the soap increased with decreasing particle size, i.e., with increasing surface area, of the carbons. The adsorption by activated charcoal was considerably higher than that obtained with even the finest of the carbon blacks.

During the course of studies in the field of detergency currently in progress in these laboratories, it became of interest to investigate the adsorption of soap on carbonaceous materials used as fiber-soiling media. A previous paper (3) gives data relating to the adsorption of various pure soaps on one carbon (standard Micronex) which may be regarded as typical of the carbons employed in detergency studies. The present paper gives data relating to the adsorption of one soap by a range of carbon blacks, differing in physical properties and method of manufacture. The results indicate that the conclusions reached with respect to the selective adsorption of fatty acid by Micronex are not specific for that carbon, but are applicable to carbon blacks in general.

Experimental

Sodium myristate that had been prepared for the previous work on the adsorption of soaps by Micronex (3) was used throughout the present work.

The carbon blacks studied are listed in Table I, the data for mean particle diameter, surface area, and structure index being obtained from manufacturers' literature (1, 2, 4).

The concept of "structure" in carbon blacks has been discussed by Sweitzer and Goodrich (2) and by Weigand (4). For many carbon blacks, certain properties, such as bulk density, sedimentation volume, liquid adsorption, and effect on the physical properties of rubber mixes, may be correlated with particle size. Such carbons are said to have a normal structure. Certain carbons, however, deviate from the normal in that they give values for the above properties that are either higher or lower than those that would be predicted from their particle sizes. "Structure index" is defined as the degree of oil adsorption (determined under standardized conditions) compared with the oil adsorption of a normal carbon of the same particle size taken as 100.

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[2] *Chemist.*

TABLE I

ADSORPTION OF SODIUM MYRISTATE BY VARIOUS CARBONS

Carbon	Mean particle diameter, mμ	Specific surface, m^2/gm [1]	Structure index	Adsorption, millimoles/gm carbon		
				No of determinations	Fatty acid	Alkali
Neo Spectra II	12.7	205	100	12	0.662±0.009	0.603±0.012
Superba	16	163	100	4	0.468±0.004	0.427±0.005
Excelsior	20	134	100	8	0.329±0.003	0.280±0.003
Standard Micronex	28	95	100	4	0.220±0.005	0.150±0.002
Statex B	31	75	100	8	0.180±0.004	0.104±0.003
Acetylene black	43	65	300	8	0.163±0.004	0.111±0.003
P-33	74	37	60	12	0.103±0.007	0.058±0.002
Lampblack	97	23	200	20	0.122±0.006	0.086±0.001
Cocoanut shell charcoal	–	–	–	4	0.980±0.002	0.466±0.005

[1] *Recalculated from manufacturers' data, which is given in acres per lb*

For purpose of comparison with the carbon blacks, adsorption measurements were also carried out on an activated cocoanut shell charcoal. This material had been steam activated, and prior to use was ball milled to pass a 200 mesh screen. The maximum particle diameter was thus about 74μ, but the available surface area was undoubtedly much larger than this diameter would indicate, owing to the porosity of the material.

The method of determining adsorption has been described previously (3). It consists essentially of shaking a weighed amount of carbon with soap solution, filtering off the carbon, and determining the fatty acid and alkali content of the filtrate.

Preliminary attempts were made to use sodium stearate as the adsorbate, since it had been shown previously that this soap is highly adsorbed by Micronex (3). However, it was found that for many of the carbons the suspending and or solubilizing power of sodium stearate was so great that clear filtrates could not be obtained. This difficulty was eliminated when sodium myristate was substituted as the adsorbate, and consequently this soap was used throughout the present work.

The adsorption of sodium myristate from 0.1% aqueous solution at 70° C. was determined for each of the carbons. Prior to the adsorption measurements the carbons were tested for extractable acid or alkali by shaking with boiled out distilled water in a manner similar to that employed in the adsorption measurements, filtering off the carbon, and determining the acid or alkali content of the filtrate. No titratable amount of acid or alkali was obtained from any of the carbon blacks, but the cocoanut shell charcoal gave an amount of alkali equivalent to 0.149 millimole per gram. The value for the adsorption of alkali from soap solution was therefore low by this amount, and was corrected by adding 0.149 to the apparent adsorption obtained. The results are given in Table I and Fig. 1.

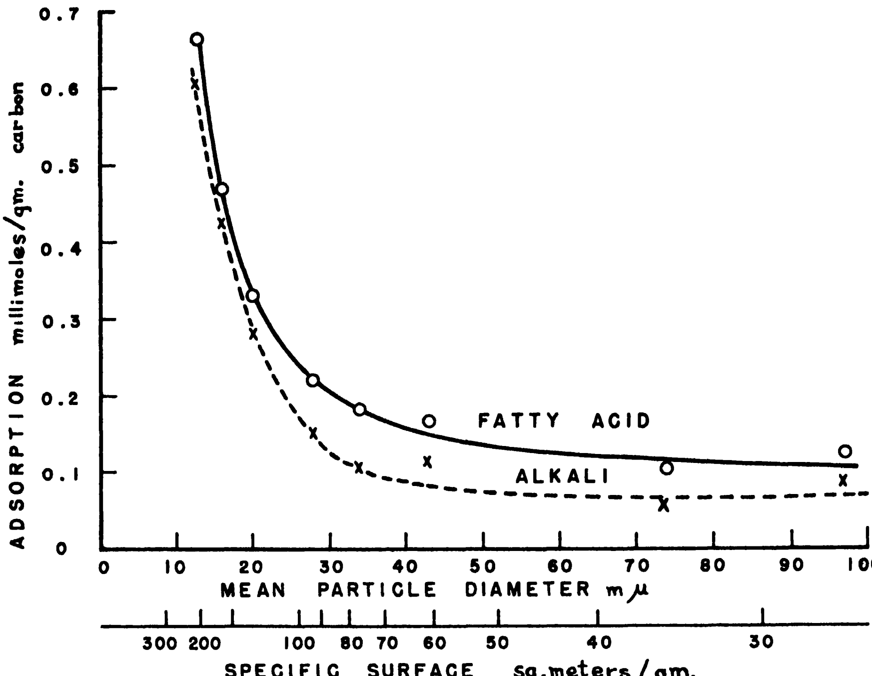

FIG. 1

Discussion

In every case the adsorption of the fatty acid component of the soap was greater than that of the alkali component. This is in agreement with data previously obtained for Micronex (3), and indicates that this property is not specific for Micronex but is characteristic of carbonaceous materials in general.

The adsorption of both fatty acid and alkali increases in a regular manner as the particle diameter becomes smaller, i.e., as the surface area becomes greater. It is interesting to note that the adsorption of both components of the soap by the high structure carbons acetylene black and lampblack falls above the curve for the normal structure carbons, whereas the adsorption by the low structure carbon P-33 falls below it. This is in accord with the foregoing discussion of carbon structure.

The adsorption of soap by cocoanut shell charcoal was considerably higher than that obtained with any of the carbon blacks. This may be attributed to the porous nature of the material resulting in a very large specific surface.

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THE "BROWNING REACTION" IN DRIED MILK POWDER[1]

By J. B. Moster[2] and R. A. Chapman[3]

Abstract

Heated and stored dried milk powders showed a marked loss of amino nitrogen as determined by the Van Slyke volumetric method, but no loss was observed when the formol titration was used. Titration curves of the powders suggested a mechanism for the protein sugar condensation. The heating of synthetic mixtures of amino acids and lactose resulted in intense browning, accompanied by a loss of amino nitrogen when a large excess of lactose was employed but no loss occurred when equal parts of sugar and amino acid were present.

Introduction

The technique of preserving food by drying has improved rapidly during the past decade. However, even modern processing methods do not prevent deterioration of dehydrated foods for indefinite periods. This instability has been particularly apparent under the drastic conditions encountered by the armed services and consequently a considerable amount of research is being conducted in this field. The present investigation was undertaken to study the chemical processes involved in the "browning reaction" in dried milk powder, since an understanding of the fundamental nature of the reaction should be of value in preventing its occurrence.

Kass and Palmer (3) and Joslyn (2) have reviewed the "browning reaction" in food products. These papers revealed that some investigators have found evidence of the formation of a protein–sugar complex. Other workers have been unable to detect any decrease in amino nitrogen after browning had occurred, and they have concluded that the reaction involves a protein-catalyzed degradation of the sugar followed by a physical adsorption of the breakdown products on the protein.

Lea and White (5) have recently reported a loss of amino nitrogen during storage of dried milk powder as determined by both the Van Slyke volumetric and the formol titration methods. The decrease was significantly greater when the Van Slyke technique was employed. These workers have suggested that the basic character of the amino group may not be sufficiently weakened by the initial reaction it undergoes during deterioration of the powder to prevent partial titration under the conditions of the formol estimations.

[1] *Manuscript received July 9, 1949.*
Contribution from the Department of Chemistry, Faculty of Agriculture (McGill University), Macdonald College, Que. Macdonald College Journal Series No. 255. This paper reports research undertaken in co-operation with the Quartermaster Food and Container Institute for the Armed Forces (United States) and has been assigned No. 263 in the series of papers approved for publication. The views or conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or indorsement of the Department of the Army.

[2] *Swift Canadian Company Research Fellow. Present address: Department of Agricultural Chemistry, Purdue University, Lafayette, Indiana, U.S.A.*
[3] *Assistant Professor of Chemistry. Present address: Food and Drugs Division, Department of National Health and Welfare, Ottawa, Canada.*

In general the results obtained in this investigation confirm those of Lea (4) and Lea and White (5). In addition, information has been obtained, which, it is believed, will further elucidate the "browning reaction".

Experimental

Amino nitrogen was determined by the Van Slyke volumetric and the formol titration methods. A 30 min. shaking period was employed, for the Van Slyke method. Milk powders, reconstituted in distilled water, tended to foam over in the gas burette of the Van Slyke apparatus when treated with glacial acetic acid and sodium nitrite Excessive foaming could be prevented by placing the reconstituted milk in a boiling water bath and agitating it vigorously with a mechanical stirrer for 15 min. This mild heating treatment did not result in any noticeable browning of the reconstituted milk, nor was there any measurable change in the formol titration values or in the dissociation properties. Ten grams of milk powder was reconstituted in about 40 ml. of distilled water and, after cooling, the volume was made up to 50 ml. Amino nitrogen was determined on 10 ml aliquots.

Levy (6) has reported that maximum accuracy in the formol titration of amino acids was obtained when neutralized formaldehyde was employed and no correction was made for a blank It was recommended that the concentration of formaldehyde should be between 6% and 9% at the end of the titration These recommendations were adopted in the present investigation The titration was carried out between pH 7.0 and pH 9.1.

Measurements of pH were made with a Beckman pH meter (Model G), equipped with a standard glass electrode assembly. The following procedure was employed. Ten grams of milk powder was reconstituted in 200 ml. of distilled water, and the pH was adjusted to 7. Sixty milliliters of neutralized 40% formaldehyde was added and the solution was titrated at 25° C. to pH 9.1, with 0.1 *N* sodium hydroxide. The solution was vigorously agitated with a mechanical stirrer while the pH readings were being made The rate of addition of the standard solution and a titration period of seven minutes were carefully controlled for all determinations.

Samples of fresh, heated, and very stale whole milk powders were examined. The heated sample was prepared by heating a fresh milk powder at 100° C. for two days. The loss of volatile substances during the heating of the powder was determined, and an amount of the heated samples equivalent to 10 gm. of the fresh sample was employed for the amino nitrogen and the titration curve experiments. Only one suitable stale sample of milk powder was available at the time of this investigation. This sample had been stored for four years in an unheated room in a container with a slip-on cover. The results of the amino nitrogen determinations are presented in Table I.

In the titration curve experiments, the milk powders were titrated at 25° C. between pH 6 and 11.3. The pH readings were taken with the same

TABLE I

THE FREE AMINO NITROGEN CONTENT OF FRESH, HEATED, AND STORED SPRAY-DRIED WHOLE MILK POWDERS

Sample	Mgm. of amino N per gm. of milk powder*	
	Van Slyke	Formol
Fresh	2.93	3.64
Heated	1.73	3.71
Stale	1.65	3.53

*Dry weight.

pH meter used for the formol titration. For all readings above pH 9, a Beckman "Type E" glass electrode was used.

In order to minimize the error caused by changes in ionic strength during titration, sufficient sodium chloride was added to the reconstituted milk to make the solution 1 *N*. The solution was titrated with 0.1 *N* sodium hydroxide to which had been added sufficient sodium chloride to make it 1 *N* with respect to the sodium ion. It was assumed that the contribution of the milk powder to the ionic strength of the reconstituted solution would not be appreciable. Since only 10 gm. was reconstituted in a liter of distilled water, the effect on the ionic strength of diluting this volume with a 100 ml. of the standard solution would be negligible.

The titration of milk powder was carried out in the following manner. Ten grams of the powder was reconstituted in 500 ml. of distilled water, 58.5 gm. of sodium chloride was added, and the volume was made up to 1 liter. The electrode was then standardized and the solutions, in turn, were adjusted to pH 6, using 1 *N* hydrochloric acid. An aliquot of standard alkali was added to each of the samples and the pH of each was taken. The electrode was then restandardized, and, if any change in asymmetry potential had occurred, the meter was readjusted and the pH of the solutions was taken again. This procedure was continued until the titrations were complete. Samples being compared were always titrated at the same time.

A blank solution, consisting of 1 liter of 1 *N* sodium chloride was titrated in a similar manner and at the same time as the milk powder samples. The volume of standard solution required to bring the blank to a particular pH was subtracted from the volume required to bring the milk powder solution to the same pH. The volumes thus obtained were then plotted against the pH values. The accuracy obtained by this method became progressively smaller as the alkalinity of the solution increased. Thus, it was found that above pH 11 it was not possible to obtain reliable results. However, this has not proved to be a serious hindrance, since a satisfactory study could be made on the portion of the curves below pH 11.

The titration curves of the milk powders are presented in Fig. 1. A number of other fresh and heated samples have been titrated, and in all cases similar results were obtained.

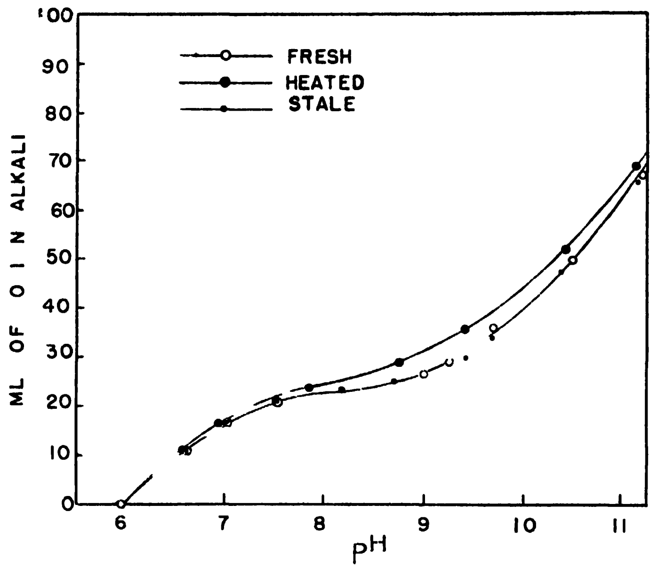

FIG. 1. *Titration curves of fresh, heated and stale milk powders (10 gm. of milk powder in 1 l. of water used in each case).*

Experiments, similar to those carried out on the milk powders, were also made on simple amino acid lactose systems. At the time that this research project was terminated, this portion of the investigation had not been satisfactorily completed. Therefore only certain parts of these experiments are being reported.

Synthetic mixtures of glycine and lactose, and lysine monohydrochloride and lactose were made up in two concentrations: (1) 1 part by weight of the amino acid to 13 parts of the sugar and (2) equal parts of each constituent. These mixtures were prepared and treated as described in Table II. In all

TABLE II

LOSS OF AMINO NITROGEN IN SYNTHETIC MIXTURES OF AMINO ACIDS AND LACTOSE

Preparation*	Treatment		% loss of amino nitrogen			
			Glycine lactose ratio by weight		Lysine HCl lactose ratio by weight	
	Temp., °C.	Time	1:13	1:1	1:13	1:1
(1)	130	2 days	20.3	0		—
(2)	100	7 hours	39.2	0	28.8	0
(3)	115	2 days	18.8	0	—	—

*(1) *Components ground together.*
(2) *Components ground together and placed in a closed vessel over a saturated solution of sodium nitrate.*
(3) *Components mixed, dissolved in distilled water, and dried from the frozen state.*

cases, control samples of amino acid alone and lactose alone were treated in a manner similar to the treatment of the synthetic mixtures. No significant browning occurred in the controls. In the mixtures, treatment with moist heat produced the darkest samples, the lyophilized samples were intermediate, and the mixtures prepared by the first method were the least discolored.

After being treated, the mixtures were dissolved in distilled water, and suitable aliquots were taken for Van Slyke amino nitrogen determinations A five minute shaking period was used for the glycine mixtures and a 20 min. period for the lysine mixtures. The results are presented in Table II.

Discussion

It is seen from the results in Table I that the amino nitrogen of the fresh sample, as determined by the volumetric technique, is about 20% lower than the value obtained by the formol titration. This difference may have been the result of an incomplete reaction between nitrous acid and the milk protein, but, more likely, was due to the fact that substances or groups, other than amino groups, were titrated in the formol titration.

The results also show that the Van Slyke volumetric technique gave much lower values for the stale and heated milk powders than for the fresh sample. However, corresponding differences were not obtained when the formol titration method was employed.

An explanation for this difference may be obtained on examination of the curves in Fig 1. It is seen that the heated powder has more titratable groups between pH 6 and 9 25. Most of these groups would be titrated in the formol titration It the number of amino groups lost during browning equalled the number of new titratable groups formed, then the formol titration would not indicate any loss of amino nitrogen. The results described may be explained by assuming that the "browning reaction" involves a condensation of the free amino groups of the milk protein with either lactose or decomposition products of lactose, to form a compound containing a secondary or tertiary amino group. The mechanism of such a condensation may be similar to the generally accepted mechanism for the reaction between formaldehyde and amino acids This reaction, proposed by Balson and Lawson (1) and Levy and Silberman (7), is represented by the following equation:

$$R\,NH_2 + CH_2O \rightleftharpoons \underset{\text{Compound A}}{R\,NH\,CH_2OH} + CH_2O \rightarrow \underset{\text{Compound B}}{R\,N\,(CH_2OH)_2} \qquad (1)$$

It is usually considered that the majority of the free amino groups of milk protein are ε-amino groups of lysine. The pK' value of this group is 10.5. By the mechanism suggested, for every ε-amino group reacting, a less basic group would be formed. This would account for the additional titratable groups observed between pH 6 and 9.25 in the heated milk powder.

The dissociation properties of the condensation products corresponding to compounds A and B in Equation (1), would depend on the number, nature, and size of the groups that have replaced hydrogen on the nitrogen atom. Therefore, by the proposed reaction or by a reaction similar to it, it would seem possible to form a compound that would possess the same dissociation properties as the original ϵ-amino group. For this reason, the fact that the titration curves of the fresh and stale* powders are similar does not necessarily discredit the suggested mechanism.

The results in Table II show the effect of sugar concentration on the sugar–protein condensation. It is seen that browning can occur with or without any loss of amino nitrogen. Variations in the concentration of constituents, and in other simple conditions, are probably the causes of many of the discrepancies that have occurred concerning the loss of amino nitrogen during browning of food products.

Acknowledgments

The authors wish to thank Dr. R. H. Common for his helpful advice in the preparation of the manuscript.

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* *One other stale powder was investigated. The results of the Van Slyke and formol amino nitrogen and titration curve experiments were very similar to the results obtained with the* heated *powder. However, this stale powder was not a normal sample, and therefore the results are not reported. The powder had been used for some previous experiment and a number of its constituents (particularly the fat) had been removed or replaced, and other components had been added.*

THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XII. THE HIGH COMPRESSION RATIO OTTO CYCLE GAS ENGINE AND THE ADVERSE EFFECT OF HIGH JACKET TEMPERATURES ON THERMAL EFFICIENCY[1]

BY R. O. KING,[2] EDWIN J. DURAND,[3] AND J. ALEX. MORRISON[4]

Abstract

Town gas was used as the fuel for the C F R engine during a series of engine trials run at a compression ratio of 10 . 1 and at jacket temperatures of 140°, 212°, 302°, and 351° F. The mixture strength at each jacket temperature was varied from the weakest to the richest on which the engine would run steadily. The object of the trials was (1) to determine the effect of jacket temperature on thermal efficiency and (2) to compare the performance of an Otto cycle engine run at 10 . 1 compression ratio with that of a compression ignition (Diesel) oil engine. The results of the trials show that thermal efficiency decreases as the jacket temperature is raised, that is, the decrease more than offsets the gain due to decrease of heat loss during combustion and expansion. It is indicated by the character of the results and by experiments described earlier that the observed loss of efficiency is due to flameless surface combustion of the fuel during compression. The performance of the C F R engine running on town gas at 10 1 compression ratio as compared with that of a compression ignition oil engine running at 12 1 was superior in respect of maximum power (I M E P) developed and range of quality control and not greatly inferior in respect of thermal efficiency.

Introduction

It was shown by experiments described in Part VI (3) that town gas, containing hydrogen in large concentration, could be used as fuel for an Otto cycle engine at compression ratios as high as 10 · 1, if precautions were taken to prevent the accumulation in the combustion space of finely divided carbon arising from pyrolysis of the lubricating oil. The power measurements made during the experiments were of a preliminary character but sufficed to show that the increase of compression ratio beyond the 5 · 1 commonly used, made possible by avoidance of nuclear ignition, was accompanied by a commensurate increase in power and thermal efficiency.

The C F R knock testing engine, belt-connected to a d-c generator, was used for the experiments mentioned. Measurements of power output and friction loss were made consequently by indirect methods and accuracy suffered accordingly. The experimental results of this Part were obtained after a swinging field electric dynamometer had been direct connected to

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Contribution from Defence Research Board (Canada) in association with the Department of Mechanical Engineering, University of Toronto
[2] *Research Scientist, Defence Research Board and Honorary Lecturer, Department of Mechanical Engineering, University of Toronto. Lately Director of Scientific Research and Development, Royal Canadian Navy*
[3] *Lecturer, Department of Mechanical Engineering, University of Toronto.*
[4] *Supervisor of Appliance Laboratory, Consumers' Gas Co, Toronto.*

the engine, and it is considered that an acceptable accuracy of measurement was attained

The objectives of the experiments were, (1) to determine if flameless surface combustion during compression would more than offset the gain in thermal efficiency due to raising the jacket temperature and (2) to obtain reliable data for an Otto cycle engine running on town gas at a compression ratio of 10 1 for a comparison of the performance with that of a compression ignition (Diesel) engine, in respect of power, efficiency, and range of quality control.

Trials were carried out with the jacket coolant at temperatures of 140°, 212°, 302°, and 351° F, mixture strength being varied over the greatest possible range and optimum ignition timing always being used The temperature of 140° F can be taken as that of the jacket coolant in motor car engines 212° F is the jacket coolant temperature of the A S T M C F R method of knock testing the higher temperatures of 302° and 351° F represent jacket coolant temperatures of liquid cooled aircraft engines The cylinders of air cooled engines attain even higher temperatures

Experimental Arrangements and Results

The C F R engine, which had been used for some weeks for fuel testing, was dismantled and all carbon and other deposits removed from combustion chamber surfaces The combustion space was maintained sufficiently free of the accumulations of finely divided carbon, which promote pre ignition and detonation, by the cleaning routine described in Parts V (2) and VI (3)

The valves were refaced and hand lapped into the seats The piston rings were in good condition and free in the grooves, all of which were clean The ignition system was checked and the breaker points set to the standard 0 020 in gap The spark plug was cleaned and the gap reduced from 0 025 in to 0 012 in as had been found necessary in earlier experiments at the high compression ratio of 10 1 The setting of the micrometer used for measuring compression ratio was checked, and maximum compression pressures corresponding to compression ratio settings were found to be in agreement with standard C F R values The maximum compression pressure at 10 1 compression ratio was 290 lb per sq in, measured during trials at 900 r p m and with the jacket coolant at 212° F

Lubrication

A commercial grade of lubricating oil, S A E 30, free of additives, was used for engine trials at jacket temperatures of 140° and 212° F A commercial grade of heavy duty oil, Esso S A E 50, recommended for use with Diesel engines was used for trials made with jacket temperatures of 302° and 351° F

Jacket Temperatures

The low temperature was obtained by passing tap water through the jacket. The water entered at the lower end of the jacket at 60° F. and flow was

regulated to maintain a nearly constant outlet temperature of 140° F. The standard evaporative method of cooling, using water, was employed to obtain a jacket temperature of 212° F. The higher jacket temperatures of 302° and 351° were obtained by evaporative cooling, using ethylene glycol suitably diluted with water, an extra section being fitted to the reflux condenser.

Power Measurement

The belt driven main and auxiliary generators of the C.F.R. unit were disconnected from the engine. The main generator was then driven as a motor from the laboratory d-c. supply and it in turn drove the auxiliary generator which supplies current for engine auxiliaries, such as the bouncing pin and the ignition system. The engine was then direct connected to a d-c. swinging field dynamometer with beam type scale. Thus, brake horsepower was measured. Indicated horsepower was obtained by adding to the observed B.H.P. that required to overcome friction and pumping losses when fuel was not added to the air supply and the engine "motored" by the dynamometer. "Motoring" loss was measured after every set of power observations as soon as possible after stopping the fuel supply. A set of observations comprised 6 power measurements made to determine optimum ignition timing for any particular rate of gas supply (mixture strength). Average values of the horsepower absorbed by friction and pumping losses, described hereafter as L.H.P., were as below,—

140° F. jacket, S.A.E. 30 oil	1.45 L.H.P.
212° F. jacket, S.A.E. 30 oil-	1.31 "
300° F. jacket, S.A.E. 50 oil—	1.24 "
350° F. jacket, S.A.E. 50 oil	1.17 "

The relatively great loss at 140° F. jacket temperature is due to the entrance of tap water into the lower end of the cylinder jacket at 60° F.

Measurement of Rate of Gas Consumption

Measurements were made by members of the technical staff of the Consumers' Gas Company of Toronto, using a standard dry meter especially fitted and calibrated for accurate measurement.

Calorific Value of the Town Gas

The composition and calorific value of Toronto town gas are closely controlled. The composition remained constant during the engine trials at jacket temperatures of 212° F. and higher, made on successive days, but differed slightly from that during the trial at 140° F. jacket temperature made some weeks earlier, as shown by the data of Table I.

The higher calorific value of the gas used for the trial at 140° F. jacket temperature, determined by calorimeter in the Gas Company laboratory, was 465.1 B.t.u. per cu. ft. and the corresponding lower calorific value obtained by calculation was 422.2 B.t.u. per cu. ft. Values obtained similarly for the gas when used later at the higher jacket temperatures were 470 and 427

TABLE I

COMPOSITION OF TORONTO TOWN GAS AT TIMES OF ENGINE TRIALS; PERCENTAGE VOLUMES

Constituents	Trial at 140° F., jacket temperature	Trials at higher jacket temperatures
Hydrogen	48.3	47.4
Carbon monoxide	23.3	21.7
Methane	11.0	12.4
Nitrogen	7.1	7.6
Carbon dioxide	3.7	4.2
Ethylene	3.0	3.8
Ethane	1.8	1.3
Benzene	1.1	0.9
Oxygen	0.8	0.7

B.t.u. per cu. ft. The "lower" values were used for calculating indicated thermal efficiency. All are for the gas at 60° F. and 30 in. of mercury.

Carburetor Arrangement

The method of admitting gas to the C.F.R. carburetor as used in preliminary experiments is shown by Fig. 1 of Part VI (3). The open end of the gas admission tube was fully exposed to the air oscillations in the induction system of the engine. The oscillations were probably without effect on the accuracy of the gas meter, but as a precaution the open end of the tube was closed and the gas passed through three rings of small holes in the wall of the tube. The air heater of the C.F.R. engine was left in place and provided a mixing chamber for the gas and air.

Ignition Timing for Maximum Power

The required ignition timing at constant engine speed and compression ratio varies with jacket temperature and mixture strength. Air and gas were both supplied to the engine at atmospheric pressure. The ignition advance required for the maximum power obtainable for a particular rate of gas consumption can be determined only by experiment. Thus the brake horsepower developed when a particular mixture was used was measured at a series of ignition timings giving rising and falling power. The optimum timing was then obtained from a plot of the results.

The method is illustrated by the graphs of Fig. 1, plotted to determine the optimum ignition timing for 14 rates of gas consumption ranging from that required for the weakest to the richest mixtures on which the engine would run steadily. It will be seen by reference to the graphs that optimum ignition timing varies over a wide range, and is somewhat sharply defined at any particular mixture strength. Thus at the weakest mixture on which the engine would run continuously, given by a rate of gas consumption of 47.5 cu. ft. per hr., optimum timing was 44° advance and output was 1.92 B.H.P. The maximum power output of 4.06 B.H.P. was obtained at a rate of gas consumption of 92.5 cu. ft. per hr., and optimum ignition timing was then 13.5° advance. The graphs for mixtures richer than that required for maxi-

mum power are given separately in the right hand top corner of Fig. 1 to save confusion. They show, as usually found, that optimum ignition timing varies less with mixture strength on the rich than on the weak side of the maximum power mixture strength.

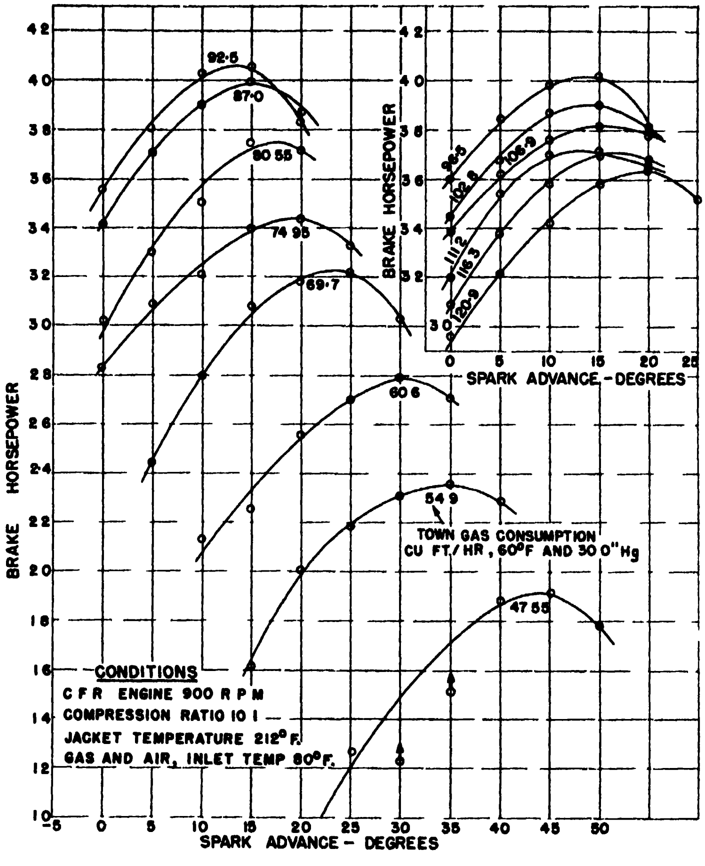

FIG. 1 *Graphs for the determination of optimum ignition timing for each of the 14 rates of gas consumption required for the set of trials made at a jacket coolant temperature of 212° F*

The experimental results required for the graphs of Fig. 1 were obtained when the jacket coolant temperature was 212° F. Similar sets of graphs were obtained for jacket coolant temperatures of 302° and 351° F. and for a jacket coolant temperature (outlet) of 140° F.

Brake and Indicated Horsepower, Mechanical Efficiency, 212° F. Jacket Coolant Temperature, Optimum Spark Advance

The experimental results given by the graphs of Fig. 1 were used to plot the graphs of Fig. 2. Graph *A* of the figure gives the relation between optimum spark advance and rate of gas consumption and Graph *B* the corresponding brake horsepower. Graph *C*, for indicated horsepower, represents the brake horsepower plus the horsepower (L.H.P.) lost in overcoming mechan-

ical and fluid friction, amounting to 1.31 B.H.P. at the jacket coolant temperature of 212° F. Graph *D*, for mechanical efficiency, gives the percentage relation of brake to indicated horsepower. It will be noted that the value at maximum power output is approximately 76%, a reasonable value in view of the engine's not having been designed for high output and low friction loss.

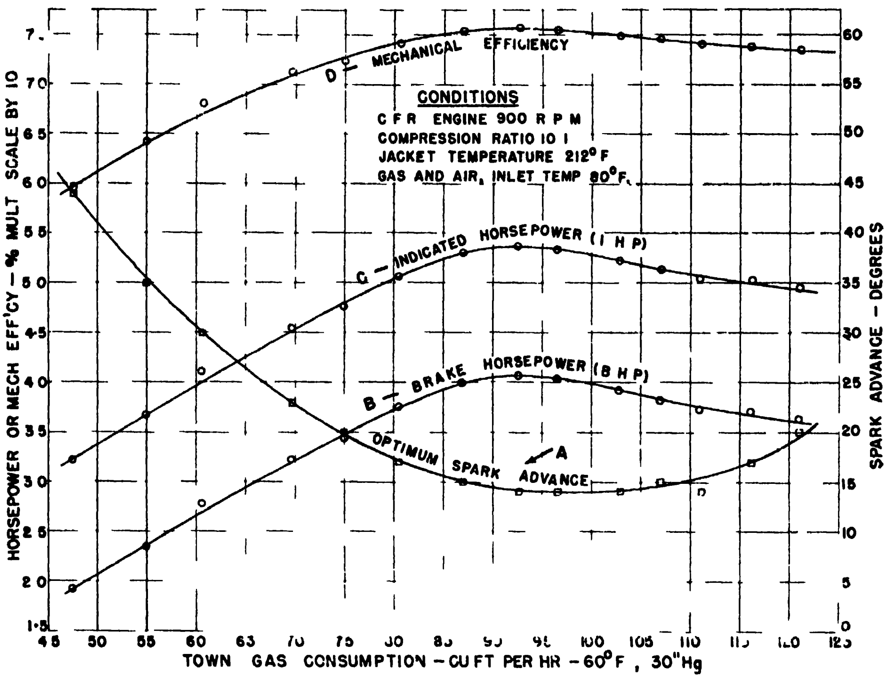

FIG. 2. *Mechanical efficiency and brake and indicated horsepower at optimum spark advance—jacket coolant, 212° F.*

Indicated or brake mean effective pressures can be obtained by multiplying values given by Graphs *C* and *B* by the factor 23.4. Thus I.M.E.P. at maximum power output was 125 lb. per sq. in.

Indicated Thermal Efficiency and Power

The internal combustion engine, being noncondensing, is restricted to converting into work some part only of the "lower" heat value of the fuel used. It is necessary therefore to use that value for calculations of thermal efficiency if comparable results for a variety of fuels are to be obtained, because the difference between the lower and higher values varies with the nature of the fuel.

Similarly, when the efficiencies of a variety of engines are compared it is necessary to take into account the total power developed, because the fraction used in overcoming friction varies with design and operating conditions. The total is represented by the indicated horsepower or by the indicated mean effective pressure.

Thus, considering as an example a particular set of engine trials at 900 r.p.m., the jacket coolant at 212° F. and compression ratio 10 : 1, the data used for the calculation of indicated thermal efficiency were as follows,—

Metered rate of gas consumption, 96.6 cu. ft. per hr.
Lower calorific value of the gas at 60° F. (520° R) and 30 in. of mercury barometric pressure, 422 B.t.u. per cu. ft.
Gas temperature at meter, 73.7° F. (533.7° R.)
Barometric pressure, corrected for temperature, 29.33 in. of mercury
Brake horsepower by dynamometer, 4.06
Friction horsepower (L.H.P.) by dynamometer, 1.31
Indicated horsepower by addition, 5.37

The rate of heat input to the engine is then,

$$422 \times \frac{520}{533} \times \frac{29.3}{30.0} \times \frac{96.6}{60} = 646 \text{ B.t.u. per min.}$$

and the equivalent ft. lb./ per min. = 646×778

The rate at which heat is converted into work is

I.H.P. $(5.37) \times 33000$, ft. lb. / per min.

and per cent indicated thermal efficiency

$$= 100 \times \frac{5.37 \times 33000}{646 \times 778} = 35.2$$

Collected Results of Engine Trials

The results of trials made with a jacket coolant temperature of 212° F. are given by the graphs of Fig. 3. They are plotted on a brake horsepower base extending from the minimum power at which the engine would run steadily to the maximum power that the engine would develop. The obtainable range of B.H.P. is shown by the vertical broken lines. It will be noted that power reaches a maximum for a particular rate of gas consumption and then diminishes as the rate is further increased. Thus the familiar consumption "loop" is obtained.

Indicated thermal efficiency attains relatively high values at weak mixtures, decreases slowly until the mixture strength for maximum power is reached, and then very rapidly with further increase in mixture strength. Then as power decreases at the same time, an indicated thermal efficiency "loop", as shown by the relevant graph of the figure, is obtained.

The results of trials made with a jacket temperature of 351° F. are presented similarly by the graphs of Fig. 4. The similar graphs for trials made at 140° and 302° F. are not reproduced because of space limitation.

The features of special interest in respect of the trials made at the four jacket coolant temperatures of the experiments are exhibited by the graphs of Fig. 5. The *A* graphs are consumption loops, and *B* graphs indicated thermal efficiency loops. They show in a striking way the progressive de-

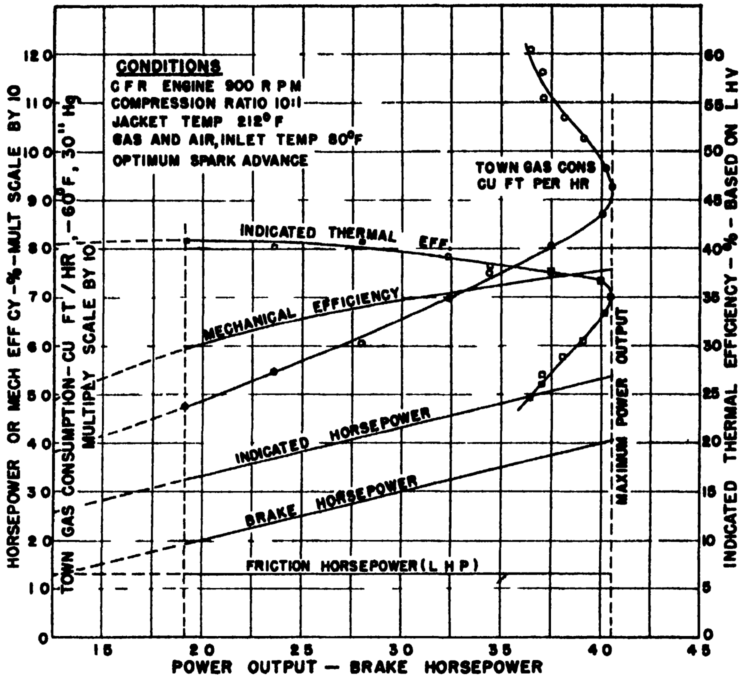

FIG 3 *Graphical presentation of the results of trials made with the jacket coolant at 212° F*

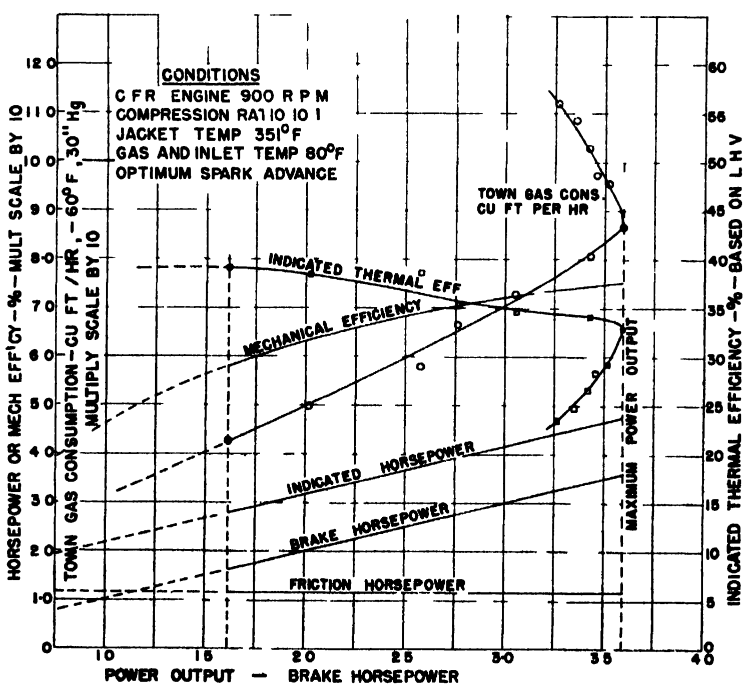

FIG 4 *Graphical presentation of the results of trials made with the jacket coolant at 351° F*

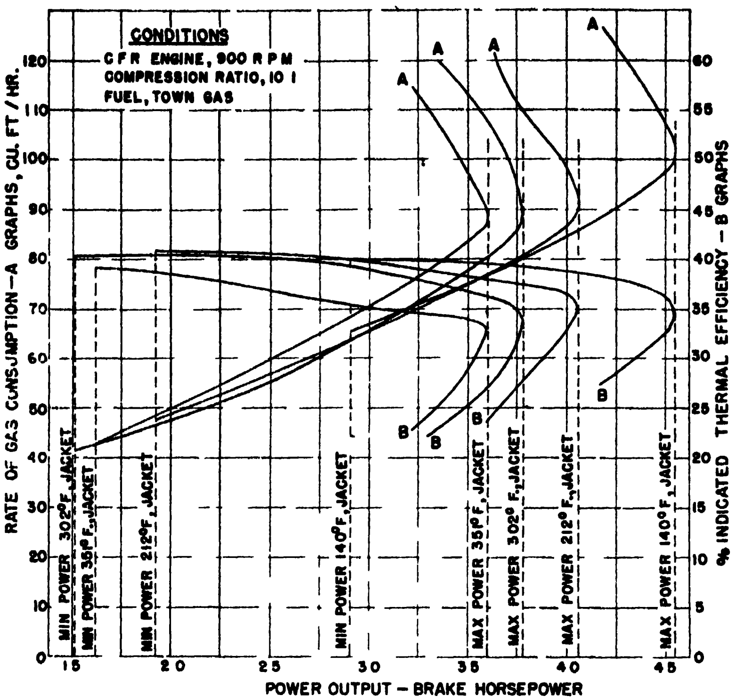

FIG 5 *Consumption loops given by A graphs and indicated thermal efficiency loops by B graphs, for trials made with jacket coolant temperatures of 140°, 212°, 302°, and 351° F*

crease of indicated thermal efficiency and power as jacket coolant temperature is raised from 140° to 351° F. Maximum and minimum powers obtained for each jacket coolant temperature are shown by the vertical broken lines. It will be noted that a relatively high value of minimum power was obtained when the jacket coolant temperature was 140° F This anomalous result is thought to be due to ignition failure at weaker mixtures.

Summary and Discussion of Experimental Results

It was not considered possible, prior to the experiments described in Parts V (2) and VI (3), to operate an Otto cycle engine on hydrogen or town gas at a compression ratio of 10 1, except when using weak mixtures and consequently obtaining relatively low values of mean effective pressure Thus, there are not extant any engine trial results for Otto cycle engines with which the experimental results given in this Part can be compared. Recourse must therefore be to the trial results of the compression ignition type of the Diesel engine. The most comprehensive described trials of that type of engine are, so far as known, those by H. B. Taylor (8, pp. 35-85). Data are given for trials run at 12 : 1 compression ratio and speeds of 800 and 1000 r.p.m. and with injection timing fixed or advanced progressively with decrease in mixture

strength. A comparison of the C.F.R. Otto cycle engine trial results with those given by Taylor for the compression ignition engine are therefore of interest although weighted in favor of the latter by the higher compression ratio of 12 : 1 at which they were run. The temperature of the jacket coolant is not mentioned in Taylor's paper but can be assumed to have been that generally used, namely, 60° C. (140° F.).

Thermal Efficiency as Affected by Jacket Temperature

An increase in jacket temperature, by diminishing heat loss during the combustion and expansion periods, should give rise to a small increase in thermal efficiency. The possibility that the increase might be more than offset by the adverse effect of surface oxidation of the fuel has not heretofore been considered, the established (textbook) view being that "no significant surface reaction occurs in the engine" (1, p. 2934).

The adverse effect of flameless surface combustion on the power developed by an Otto cycle engine running on gasoline was shown by the experiments described in Part XI (4). The experiments of this Part were made to determine if a similar effect would be obtained in suitable conditions if the engine were run on town gas containing a large proportion of hydrogen, which reacts with metallic oxide at relatively low temperatures to form steam. The experimental results obtained accordingly are summarized in Table II. The data given for jacket coolant temperatures of 212° F. are from the graphs of Figs. 2 and 3. The data relating to other jacket coolant temperatures are from similar graphs, which are not reproduced because of space limitations.

TABLE II

INDICATED THERMAL EFFICIENCY AND INDICATED MEAN EFFECTIVE PRESSURE AS AFFECTED BY JACKET COOLANT TEMPERATURE

Jacket coolant temperature, °F	Max. power		75% max power		Min power	
	I.M.E.P., lb./sq. in.	I.T.E., %	I.M.E.P., lb./sq. in.	I.T.E., %	I.M.E.P., lb./sq. in.	I.T.E., %
140	140.4	35	105	40	(102)	(40)
212	125.0	35	91	40	76	41
302	117.0	33.5	88	40	65	40
351	111.0	32.5	83	37	65	39

With reference to Table II, consider first the effect on thermal efficiency of raising the jacket temperature from 140° to 212° F. The estimates by Ricardo (6, p. 87) and Ricardo and Glyde (7, p. 103), which are not based on experiment, led to the conclusion that an increase of from 0.4% to 1.0% would be obtained. This no doubt is an accurate estimate, taking into account heat loss only. The *experimental* results given in Table II show, however, that no change in thermal efficiency occurred within the jacket coolant temperature range 140° to 212° F., the minimum power measurements at 140° F. being disregarded, for the reason already mentioned. It may be

concluded accordingly that the gain due to the lower heat loss during combustion and expansion was just equal to the loss due to surface oxidation of the fuel during compression.

Consider now the effect on efficiency of raising the jacket coolant temperature from 212° to 351° F. There should, of course, be a gain in thermal efficiency due to lower heat loss to the jacket but instead efficiency decreases by 7% at maximum power and by 7½% at three-quarter power. The total loss attributable to surface oxidation would therefore be the sum of the percentages mentioned plus whatever gain there might have been, taking into account the lower heat loss to the jacket.

The smaller efficiency loss of 4.9%, observed when using the weak mixture required for minimum power, is attributed to the decrease in velocity of the surface reaction with decrease in mixture strength.

Thermal Efficiency, Weak Mixtures

Thermal efficiency should, according to generally accepted theory, approach the Air Standard value as the concentration of fuel in the mixture with air approaches zero. The experimental results obtained with the C.F.R. engine running at 10 : 1 compression ratio indicate, on the contrary, that thermal efficiency attains a maximum value at a mixture strength richer than the weakest on which the engine continues to run. A similar effect was obtained as a result of earlier experiments with town gas [Part VI (3)]. The observed decreases from the maximum, although small, are of sufficient interest to justify further experiments.

Quality Control

A feature of the Diesel or compression ignition type of Diesel is that power output at any particular speed can be varied over a wide range by varying the rate of fuel supply, that is, the "quality" of the fuel–air mixture. It became of interest, therefore, to determine the degree of quality control obtained when the C.F.R. engine was run at 10 : 1 compression ratio and with jacket coolant temperature varied over a wide range.

Percentage quality control is taken to be:—

$$\frac{\text{Maximum B.H.P.} - \text{Minimum B.H.P.}}{\text{Maximum B.H.P.}} \times 100$$

Relevant data from the C.F.R. engine experiments are set out in Table III.

TABLE III

QUALITY CONTROL DATA, C.F.R. ENGINE
10 : 1 COMPRESSION RATIO

Temperature of jacket coolant, °F.	Max. B.H.P.	Min. B.H.P.	Friction H.P.	Percent Q control
140	4.55	2.91	1.35	36
212	4.05	1.91	1.31	53
302	3.76	1.52	1.24	60
351	3.60	1.61	1.17	55

The relatively low percentage quality control at 140° F. jacket coolant temperature is believed to be due to ignition failure, as already mentioned.

The obtaining of a wide range of quality control depends on continuing ignition as mixture strength is progressively weakened. The spark ignition system of the C.F.R. engine is not especially adapted for use with very weak mixtures, and although the results are somewhat irregular, as would be expected, it is of interest to compare them with those relating to compression ignition engines as given by Taylor (8).

The percentage quality control obtainable with the compression ignition engine was found by Taylor (8) to diminish with speed and to be little affected by injection timing. Relevant data, taken from page 47 of the reference quoted, are given in Table IV.

TABLE IV

QUALITY CONTROL DATA, COMPRESSION IGNITION ENGINE, 12 : 1 COMPRESSION RATIO

Engine r.p.m.	Max. B.H.P.	Injection degrees advance	Min. B.H.P.	Injection advance	Percent Q control
800	64.6	11.5	30		54
800	65.0	12.5	30	31.5	54
1000	80.0	12.0	40		50
1000	79.5	12.0	10	29.5	50

The percentage quality control for the compression ignition engine if run at 900 r.p.m. can be taken as 52. The Otto cycle C.F.R. engine run at that speed and at the lower compression ratio of 10 : 1 affords quality control of 53, 60, and 55% for jacket temperatures of 212°, 302°, and 351° F. respectively.

Quality control is determined by the spread between maximum and minimum brake horsepower (B.M.E.P.). The minimum cannot be greater than the B.H.P. required to overcome friction and pumping losses and may be more nearly reached with the Otto cycle engine by improving spark ignition at weak mixtures. The maximum can be the greater for the Otto cycle engine because of the inability of the compression ignition engine effectively to utilize the mixture strength required for maximum power.

Volumetric Efficiency, Spark Advance

The engine was always run at constant speed and compression ratio, and any decrease in volumetric efficiency observed on raising the jacket temperature would be due to the consequent heating of the induced charge. The extent of the decrease for a particular increase of jacket temperature would depend mainly on the turbulence and thermal conductivity of the gas–air mixture entering the cylinder. The mixture enters the cylinder of the C.F.R. with a high degree of turbulence because of high velocity attained in passing through a somewhat restricted inlet valve opening, and the gas–air mixture

containing hydrogen in large proportion is of relatively high thermal conductivity. The conditions of the engine trials were therefore such that a large decrease in volumetric efficiency would be expected. Moreover, the increase in charge temperature due to increasing the jacket temperature would give rise to an increase in compression temperature, a corresponding increase in rate of flame propagation after spark ignition, and a consequent decrease in optimum spark advance. Relevant data collected from the experimental results are set out in Table V.

TABLE V

EFFECT OF JACKET TEMPERATURE ON VOLUMETRIC EFFICIENCY AND OPTIMUM SPARK ADVANCE

Jacket coolant temperature, °F	Maximum I H P	Gas consumption cu ft./hr.	Spark advance
140	6 00	102	16°
212	5 40	91 5	14°
302	5 00	88 5	8°
351	4 75	87	4°

When the engine charge is heated during induction, volumetric efficiency diminishes and indicated power decreases in the same proportion if speed and compression ratio remain constant, according to a discussion by Pye (5, p. 240), of experiments by Ricardo. On this basis the decrease of maximum I.H.P. from 6.00 to 4.75, Table V, indicates a large decrease of 20.8% in volumetric efficiency. The method of calculation is based necessarily on the generally accepted view that indicated thermal efficiency does not *diminish* with increase of jacket temperature. It has been shown, however, Table II, that a decrease of 7% was obtained on increasing jacket coolant temperature from 140° to 351° F. Thus of the total decrease of 20 8% in I.H.P , 13.8% represents that due to decrease of volumetric efficiency.

The change in volumetric efficiency can be calculated by another method. Thus, when the engine charge is gas and air, both being supplied at the same temperature and pressure, the rate of consumption of either is proportional to volumetric efficiency *if mixture strength remain constant.* It may safely be assumed that the mixture strength for maximum power is invariable. With reference to Table V, rate of gas consumption at maximum power diminishes from 102 to 87 cu. ft. per hr., that is, by 14.7% when the jacket coolant temperature is raised from 140° to 351° F. The decrease in volumetric efficiency of 14.7% agrees as well as could be expected with the value of 13.8% deduced from observed changes in power and efficiency.

Optimum Ignition Timing

The decrease in optimum spark advance as jacket temperature is raised is given in Table V and reflects the increase in rate of flame propagation as compression temperature increases with increase in the temperature of the gas–air mixture at the beginning of compression. The result, so far as engine

operation is concerned, is that the usual effects of excessive spark advance, namely, loss of power accompanied by rough running and knock, are obtained for a relatively small advance beyond the optimum value.

Concluding Comment

The Adverse Effect of Surface Combustion on Thermal Efficiency

The decrease of thermal efficiency obtained on raising the temperature of the jacket coolant of the C.F.R. engine is attributed to the effect of flameless combustion of hydrogen on oxide coated surfaces, to produce steam during compression. The decrease of efficiency becomes greater as mixture strength increases because the velocity of the surface reaction increases accordingly. Thus the decrease in indicated thermal efficiency, Table II, is 7% at the mixture strength for maximum power. It is 10.3%, that is, 50% greater for the richer mixture obtained on increasing rate of gas consumption by 20%. The adverse effect on thermal efficiency due to surface oxidation is similar to that described in Part XI (4), obtained when surface oxidation of liquid fuel vapor to steam and carbon dioxide occurred on a metal surface maintained in an oxidizing atmosphere by continuous decomposition of a metallic antiknock.

It is to be noted that the conclusion in respect of the cause of the decrease in thermal efficiency with increase in jacket temperature is based on the somewhat indirect evidence afforded by earlier experiments, mainly those described in Part XI (4). Further experiments made in a manner to eliminate surface combustion would therefore be of interest.

Otto Cycle Compared with Compression Ignition (Diesel) Performance

Combustion in the compression ignition (C.I.) engine leaves unused from 20 to 25% of the air in the cylinder charge. This is approximately the percentage of the air displaced when town gas in "correct" proportion with air is used as the fuel for an Otto cycle engine. Combustion of the fuel, especially when rich mixtures are used, is the more nearly complete in the Otto cycle engine because of the homogenity of the mixture with air. It would be of interest to compare performances on the basis of the same compression being used. A comparison can however be made at present on the basis of 10 : 1 compression ratio only and 900 r.p.m. for the C.F.R. Otto cycle engine and 12 : 1 compression ratio and 1000 r.p.m. for the C.I. engine. The data for the "best" performance of the C.I. engine used by Taylor (8) are given (page 47 of the reference). The maximum cylinder pressure was 800 lb. per sq. in. and injection timing was advanced as load was reduced.

The maximum I.M.E.P. obtained by Taylor was 133.7 lb. per sq. in., with an indicated thermal efficiency of 38.3%. The corresponding figures for the C.F.R. Otto cycle engine were 140.4 and 35%.

The I.M.E.P. obtained by Taylor at the weakest usable mixture strength was 77.5 lb. per sq. in. with an indicated thermal efficiency of 46.4%. The

corresponding figures for the C.F.R. engine were (at 212° F. jacket temperature) 76 lb. and 41%.

The C.F.R. Otto cycle engine was somewhat superior in respect of the important feature of quality control, as shown by the data of Tables III and IV.

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RELATIONS OF THIAMINE CONTENT IN SASKATCHEWAN WHEAT TO PROTEIN CONTENT, VARIETY, AND SOIL ZONE[1]

By E. Y. Spencer[2] and M. W. Galgan[3]

Abstract

The thiamine content (by a short method) and the protein content of 754 samples of the 1946 wheat crop and 458 samples of the 1947 wheat crop were determined. In 1946 four varieties were tested in each of the four soil zones, while in 1947 three varieties were tested on the Brown and Dark Brown soils and four on the Black and Black-Gray Transition soils. A highly significant positive correlation between thiamine and protein content was found for the two crops. No significant differences between thiamine values of the Thatcher 1946 and 1947 crop were found. Similarly, an analysis of variance for thiamine content of Redman in the Black and Black-Gray Transition soil zones and Rescue in the Brown and Dark Brown soil zones, for the two crop years, showed no significant difference Of the four varieties, Thatcher, Rescue, Pelissier, and Stewart, grown in the Brown and Dark Brown soil zones, Stewart was significantly higher in thiamine content The greatest range in thiamine content was 2 73 μgm. per gm. for Thatcher in the Black-Gray Transition soil zone (mean 4 01 μgm. per gm) to 9 57 μgm per gm for Stewart in the Brown soil zone (mean 6.18 μgm per gm). A highly significant difference was found for varieties grown in different zones for both years. The values decreased as the soil changed from brown to dark brown, to black and degraded black, and finally to gray

Introduction

A collaborative study by the Universities of Manitoba, Saskatchewan, and Alberta has shown considerable variation in thiamine content in wheat (11). McElroy *et al.* (5) previously found that the thiamine content of wheat in Alberta was influenced by soil type, and there was a positive correlation between protein and thiamine content. Robinson *et al.* (8) found in the 1946 Manitoba wheat crop a varietal effect on thiamine content but the content was not determined by the soil zone in which the samples were grown No positive correlation was found between thiamine and protein content. O'Donnell and Bayfield (7) and Whiteside and Jackson (12) also found that there were differences in thiamine content of wheat due to varieties. It was felt desirable to continue the study of the varietal and zonal influences on thiamine content in Saskatchewan especially when a large number of samples of wheat from many parts of the province were available.

The use of a shorter method for thiamine determination became a necessity in order to carry out the extensive survey. Previous work (1, 2, 4) indicated the possibility of using a short method, but it was necessary to adapt it for wheat.

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[2] *Associate Professor.*
[3] *Graduate Assistant.*

Methods and Materials

The short method as adapted for thiamine determination in wheat was as follows. One gram of wheat ground to pass 1 mm. sieve openings was placed in a 50 ml. volumetric flask, and 25 ml. of sodium acetate buffer, pH 4.6, was added. The sample was digested for one hour in a water bath at 70° C.

Key to Fig 1—Soil Zones and Subzones

1 Brown Soils—	*1A*	*– Subject to frequent droughts*
	1B	*—Subject to more frequent droughts than 1A*
2 Dark Brown Soils—	*2A*	*—Subject to occasional droughts, better moisture conditions than 1A*
	2B	*—Slightly cooler than 2A*
	2C	*—Bench land, cooler, shorter frost-free season and better moisture conditions than 1A*
	2D	*—Higher elevation and distinctly shorter frost-free season than 2B*
	2E	*—Heavy clay soils, more drought resistance than 2A and 2B*
	2F	*—Heavy clay soils, more drought resistance than 1A and adjoining 2B*
3 Black Soils—	*3A*	*—Better moisture conditions than 2A*
	3B	*—Shorter frost-free period and better moisture conditions than 3A*
	3C	*—Better moisture conditions than 2B, and cooler than 3A.*
	3D	*—Better moisture conditions than 3E*
	3E	*—Shorter frost-free season and better moisture conditions than 2D*
	3F	*—Degraded black and some gray soils, shorter frost-free period than 3D.*

4A, B. Black-Gray Transition Soils—Short frost-free season

After it was brought to volume, it was centrifuged for 15 min. at 2000 r.p.m. Aliquots of 5 ml. were placed in reaction vessels, and the procedure was continued as in the regular method used in the collaborative study (11).

A comparison of the results obtained by the above short method and the regular method (11) on 59 samples of wheat was made. The coefficient of correlation (r = .81) was highly significant (1% level) and the regression equation was $E = 1.49 + 0.775\,x$, where E is the estimated value and x is the value found by the short method.

Using the short method, analyses for thiamine were made on wheat samples grown at various locations in Saskatchewan (3). The 1946 crop consisted of 754 samples of wheat including the varieties Apex, Thatcher, Redman, and Rescue, while the 1947 crop consisted of 458 samples, consisting of the varieties Thatcher, Redman, Rescue, Regent, Pelissier, and Stewart.

The cereal variety zones based on soil type and climatic condition from which wheat samples were obtained are shown in Fig. 1 (9). While this map is basically the soil zone map of Saskatchewan (6), the soil zones have been subdivided because of differences within the zones which effect cereal production but which have not in general resulted in differences in the soil profile.

Results and Discussion

The thiamine values for wheat ranged from 2.98 to 7.06 μgm. per gm. in 1946 and 2.73 to 9.57 μgm. per gm. in 1947.

The relation between protein and thiamine content was studied by grouping the values according to zones on which the samples were grown. Table I shows a highly significant positive correlation existing between protein and

TABLE I

RELATION BETWEEN PROTEIN AND THIAMINE IN WHEAT FOR 1946 AND 1947 CROP IN THE VARIOUS SOIL ZONES OF SASKATCHEWAN

Zone	D f	Protein* % (Mean)	Thiamine* μgm /gm (Mean)	Correl. coeff.	5% Level	1% Level
1946						
1 Brown	205	16.06	4.67	.21	0.137	0.180
2 Dark Brown	192	15.62	4.58	.69	0.139	0.182
3 Black	287	14.93	4.35	.58	0.116	0.160
4 Transition	66	13.70	4.10	.55	0.232	0.302
1947						
1 Brown	48	16.29	4.72	.69	0.274	0.355
2 Dark Brown	77	15.83	4.41	.34	0.220	0.286
3 Black	173	15.10	4.56	.28	0.149	0.196
4 Transition	29	14.65	4.26	.43	0.349	0.449

13.5% moisture basis.

thiamine for the 1946 crop in the four zones. Similar results were obtained from the study of protein and thiamine content for the 1947 wheat crop. The relation was further studied by grouping the samples according to varieties. Table II shows a highly significant positive correlation existing between

TABLE II

RELATION BETWEEN PROTEIN AND THIAMINE IN WHEAT FOR 1947 CROP IN REDMAN, THATCHER, RESCUE, AND REGENT

Variety	D f.	Protein,* % (Mean)	Thiamine,* μgm./gm. (Mean)	Correl. coeff.	5% Level	1% Level
Redman	68	14.80	4 58	.72	0.233	0.303
Thatcher	132	15.57	4.32	68	0.169	0.220
Rescue	62	15.76	4.56	.65	0.245	0 318
Regent	68	15.36	4.72	.66	0.233	0 303

***13.5% moisture basis.**

protein and thiamine in each of the four varieties of the 1947 crop, Redman, Thatcher, Rescue, and Regent.

In order to study the effect of varieties and soil zones on the thiamine content of wheat, the data were grouped according to variety and zone for each of the years 1946 and 1947 as shown in Tables III and IV.

TABLE III

THIAMINE CONTENT OF 1946 WHEAT GROUPED ACCORDING TO VARIETY AND SOIL ZONE

Zone	Thatcher		Redman		Rescue		Apex		Zonal mean	
1	4.60	(52)	4.99	(52)	4.52	(51)	4.56	(51)	4.67	(206)
2	4.57	(18)	4.83	(48)	4 42	(49)	4 52	(48)	4.58	(193)
3	4.29	(72)	4.52	(72)	4.24	(72)	4.34	(72)	4.35	(288)
4	4.05	(17)	4.34	(17)	4.01	(16)	4.00	(17)	4.10	(67)
Varietal mean	4.42	(189)	4.71	(189)	4 34	(188)	4.42	(188)	4.47	(754)

(Mean thiamine values in μgm. per gm., number of samples shown in brackets.)

TABLE IV

THIAMINE CONTENT OF 1947 WHEAT GROUPED ACCORDING TO VARIETY AND SOIL ZONE

Zone	Thatcher		Rescue		Pelissier		Stewart		Zonal mean	
1 Brown	4.64	(26)	4.80	(24)	4 98	(24)	6.18	(24)	5.14	(98)
2 Dark Brown	4.33	(38)	4.49	(39)	4.50	(38)	5.45	(38)	4.69	(153)
Varietal mean	4.46	(64)	4.61	(63)	4.69	(62)	5.73	(62)	4.87	(251)
	Thatcher		Redman		Regent				Zonal mean	
3 Black	4.32	(58)	4.62	(59)	4.76	(59)			4.57	(176)
4 Transition	4.01	(11)	4.37	(10)	4.49	(10)			4.28	(31)
Varietal mean	4.27	(69)	4.58	(69)	4.72	(69)			4.52	(207)

(Mean thiamine values in μgm. per gm., number of samples shown in brackets.)

It will be noted that the thiamine values were highest for Redman in all zones in 1946. In the 1947 crop, Redman samples were available only in the Black and Transition soil zones and the thiamine values for it were higher than the corresponding values for Thatcher. However, in the same zones, Regent contained the highest thiamine content. In the Brown and Dark Brown soil zones, Stewart contained considerably more thiamine than the other varieties. The thiamine content was greatest in the Brown soil zone. The lowest values were in the Black-Gray Transition soil zone. There was a decrease in thiamine content as the soil changed from brown to gray.

An analysis of variance as presented in Table V shows that the differences between varieties and zones were highly significant. Samples from each of

TABLE V

ANALYSIS OF VARIANCE FOR THIAMINE IN 1946 AND 1947 WHEAT GROUPED ACCORDING TO VARIETY AND SOIL TYPE

Source of variation	1946		1947			
	Zones 1, 2, 3, 4		Zones 1, 2		Zones 3, 4	
	D.f.	Mean sq.	D.f.	Mean sq.	D.f.	Mean sq.
Total	753		250		206	
Varieties	3	4.95**	3	21.19**	2	3.49**
Zones	3	8.09**	1	11.93**	1	2.18**
Varieties x zones	9	0.14	3	0.74	2	0.23
Error	736	0.48	240	1.09	201	0.45

***Significant beyond 1% level.*

the four zones were available for Thatcher for 1946 and 1947 (See Tables III and IV). An analysis of variance for Thatcher for each of the two years presented in Table VI shows that there was no significant difference between years, whereas there was a highly significant difference between zones. Similarly an analysis of variance for Redman in the Black and Transition soil, and Rescue in the Brown and Dark Brown soil, for 1946 and 1947, showed no significant difference between years; however, there was no significant difference between zones.

TABLE VI

ANALYSIS OF VARIANCE FOR THIAMINE IN THATCHER, REDMAN, AND RESCUE FOR 1946 AND 1947

Source of variations	Thatcher		Redman		Rescue	
	D.f.	Mean sq.	D.f.	Mean sq.	D.f.	Mean sq.
Total	321		157		162	
Years	1	0.33	1	0.39	1	0.73
Zones	3	2.98**	1	1.03	1	1.02
Error	317	0.41	155	0.46	160	0.57

***Significant beyond 1% level.*

A further relation between thiamine content and varietal and regional effects is shown in Table VII, in which the mean thiamine values of the 1947 crop were arranged according to variety and subzones. Where the subzones have been grouped together, this was done because statistical analysis showed no

TABLE VII

THIAMINE CONTENT OF WHEAT GROUPED ACCORDING TO VARIETY AND SUBZONES FOR 1947 CROP

Subzone	Thatcher		Redman		Rescue		Regent		Pelissier		Stewart		Subzonal Mean	
1A	4.35	(13)			4.28	(12)			4.42	(12)	5.58	(13)	4.67	(50)
1B	4.92	(13)			5.32	(12)			5.55	(12)	6.90	(11)	5.63	(48)
2A	4.11	(7)			4.32	(7)			4.21	(7)	4.57	(7)	4.30	(48)
2B (S)	4.39	(7)			4.54	(7)			4.50	(7)	5.48	(7)	4.73	(28)
2B (N)	4.63	(9)			4.94	(9)			5.11	(9)	6.39	(9)	5.27	(36)
2C, 2D	4.01	(8)			4.11	(8)			3.63	(7)	4.46	(7)	4.05	(30)
2E	4.45	(4)			4.31	(4)			4.40	(4)	5.31	(4)	4.62	(16)
2F	4.51	(3)			4.64	(4)			5.26	(4)	6.69	(4)	5.33	(15)
3A	4.35	(8)	4.44	(8)			4.59	(8)					4.46	(24)
3B, 3C (E)	4.22	(17)	4.42	(17)			4.57	(17)					4.41	(51)
3B, 3C (W)	4.12	(13)	4.69	(13)			4.81	(13)					4.65	(39)
3E	4.38	(17)	4.92	(16)			5.06	(17)					4.78	(50)
3F	3.90	(3)	4.45	(5)			4.45	(4)					4.31	(12)
4A, 4B	4.01	(11)	4.37	(10)			4.49	(10)					4.28	(31)
Varietal mean	4.36	(133)	4.58	(69)	4.61	(63)	4.72	(69)	4.69	(62)	5.73	(62)	4.52	(258)

(*Mean thiamine values in μgm. per gm., number of samples shown in brackets*)

differences between them. Similarly, where the subzones have been split (e.g., 2B (N) and (S)) statistical analysis indicated that there was a significant difference in the values for the regions.

Differences between zones might be attributable to either nutritional or climatic effects or both. Zonal differences in soils are present because of broad climatic differences and are reflected in the soil primarily in the amount of organic matter, soil color, and nitrogen content.

TABLE VIII

ANALYSIS OF VARIANCE FOR THIAMINE—VARIETIES AND SUBZONES—1947 CROP

Source of variation	Zone 1		Zone 2		Zone 3	
	D.f.	Mean sq.	D.f.	Mean sq.	D.f.	Mean sq.
Total	97		152		175	
Varieties	3	12.07**	3	9.86**	2	3.07**
Subzones	1	22.72**	5	6.93**	4	6.19**
Error	93	1.26	144	0.60	169	0.43

****Significant beyond 1% level.***

Differences between the subzones within one zone are largely considered by the cerealists to be due to local climatic factors which are not reflected in the soil profile, but which affect cereal production Certain exceptions do occur where soil profile differences do exist to justify the subzone separation, e.g., in the Brown soil zone the more droughty B subzone is characterized by gray-brown surface colors and lower organic matter content than the rest of the Brown soil zone (10). Similarly, the C and D subzones of the Dark Brown soil zone are dark brown primarily because of the climatic effects of higher elevations. These have been differentiated as cereal subzones because of a shorter frost-free season.

Whether the observed differences in thiamine contents between soil zones and between subzones are due primarily to nutritional factors associated with the soils, or to moisture relations associated with climate, or both, is a question that cannot be answered at this time. The available meteorological data in this region are by no means sufficient to permit any comparisons on the basis of local climates for one or two years.

The thiamine values for different varieties of wheat appear to be influenced by soil and climatic conditions. The more arid brown soils tend to produce wheat of the highest thiamine content, while the gray soils with good moisture conditions tend to produce wheat with the lowest thiamine content.

In addition, there are significant differences between the various subzones within the zones; 1B (Gray Brown) containing significantly more thiamine than 1A (Brown) and 2C and D, the Dark Brown soils of higher elevation and shorter frost-free period containing less than the rest of that zone. Similarly in the Black soil zone, significant differences exist between the regions of the zone. Whether these differences are due to climatic effects of these particular years or not is unknown owing to unavailability of adequate meteorological data. There also appears to be a consistent varietal difference in thiamine content of wheat.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXXIII. AUTOMATIC pH CONTROL IN THE DISSIMILATION OF SUCROSE BY *BACILLUS POLYMYXA*[1]

BY R. W. WATSON,[2] FLORENCE TAMBOLINE,[3] AND G. W. HARMSEN[3]

Abstract

An electronic control circuit was used to maintain pH within ± 0.02 units between successive additions of soluble alkali. Carbon balances show the effects of a series of pH levels and of a range of sucrose concentrations on the proportional yields of end products. There is a marked change in the chemical balance of this fermentation at about pH 7.0, correlated with a suppression of the acetoin enzyme system. Above pH 6.8 a sharp increase in acid production is correlated with decreased formation of diol and carbon dioxide: below pH 6.8 the yield of organic acids decreases steadily. Most efficient conversion to diol occurs from pH 6.0 to 6.4. Several reasons are advanced for selecting pH 6.2 as the optimum. Under anaerobic conditions the fermentation rate is increased over that under aerobic conditions. Diol yields increase and ethanol yields decrease steadily with increasing sucrose concentrations. The increases in diol are accompanied by decreasing yields of organic acids, and not by changes in carbon dioxide production, which remains relatively uniform. The sucrose concentration most efficient for conversion to diol is about 8%, which is dissimilated anaerobically in 30 hr. at pH 6.2 to yield 65 mM (millimoles) of diol per 100 mM. of invert sugar fermented. Under aerobic conditions the diol-ethanol ratios show a marked increase, and reach a maximum of about 11 at 10% sucrose. This is due largely to increased acetoin and decreased ethanol formation. The dissimilation of 6% sucrose reaches 98% in 71 hr. under aerobic conditions and yields 82 mM. of diol plus acetoin per 100 mM. of invert sugar fermented. The use of either sodium or potassium hydroxide in place of ammonium hydroxide increases five times the period for complete dissimilation of 5% sucrose. Advantages of controlling the reaction by addition of ammonium hydroxide are reviewed.

Introduction

Continuous precise control of pH at an optimal level by the addition of soluble alkali to fermentation media has been found to increase markedly the rate of carbohydrate dissimilation by bacteria (24, 25, 26, 33). Selection of the optimum pH for the formation of a given product enables a maximum yield to be obtained in a minimum time. It is the purpose of this investigation to establish the optimum pH for the production of D-(*levo*)-2,3-butanediol

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[2] *Biochemist, Industrial Utilization Investigations.*
[3] *Bacteriologist, Industrial Utilization Investigations.*

(30) from sucrose and to determine the effects of various sucrose concentrations on fermentation times and product yields under aerobic and anaerobic conditions.

Automatic pH control was first successfully applied to small volumes of fermentation media by Longsworth and MacInnes in their study of the dissimilation of galactose by *Lactobacillus acidophilus* (24). A reliable electronic monitor, differing widely from that used by Longsworth and MacInnes, has recently been produced in these laboratories. The initial impetus in the development of this instrument was provided by Ledingham *et al.* (23). Contributions to its design were made by various members of the Radio and Electrical Engineering Division, and the electronic control circuit has recently been described by Breeze (5, 6). Neish and Ledingham devised accessory apparatus and were the first to use the monitor in studies of the dissimilation of glucose by *Aerobacter aerogenes*, *Bacillus polymyxa*, *Serratia marcescens*, and *Bacillus subtilis* (33). In the belief that the recent three-channel model (6) may be of value in a wide range of chemical and biochemical studies, further information regarding its use is given in this communication.

The production of *levo*-2,3-butanediol by the fermentation of whole wheat mashes, starch, and whole barley has been the subject of numerous investigations. The ability of *B. polymyxa* to ferment starch without preliminary saccharification led to the early utilization of whole wheat (1, 16, 22, 23, 47). Attention was later turned to the use of starch (10, 17, 18) and of ground barley (42). In a further search for more economical source materials, the fermentation of beet molasses has been undertaken in these laboratories on a pilot plant scale. The present study provides information that may serve as a basis for the utilization of molasses.

Experimental

Two locally isolated strains of *B. polymyxa* (C3(2) and C42(3)) and one strain originally obtained from the University of Alberta (UA206) were selected for their high yields of 2,3-butanediol. Studies of the rate of fermentation of 15% whole wheat mashes by C3(2) showed it to be among the four best strains on the basis of diol and ethanol yields (23). Strain C42(3) has given consistently good results with wheat (12) and through the kindness of Mr. F. J. Simpson a promising variant (E13) of C42(3) was obtained from the pilot plant. This variant had been isolated during the course of studies on the adaptation of strains of *B. polymyxa* to the fermentation of molasses, and was selected for its high production of 2,3-butanediol from this substrate.

The complex nitrogen and growth factor requirements of *B. polymyxa* were found by Katznelson and Lochhead (19) to be best supplied by a basic medium containing yeast extract, glucose, and inorganic salts. Reagent sucrose (Merck's and Baker and Adamson's), yeast extract (Difco), and nutrient salt solutions were sterilized in four separate portions to give on mixing 250 ml. of a medium containing varying concentrations of sucrose, 0.5% yeast extract,

0.05% dipotassium hydrogen phosphate, 0.05% potassium dihydrogen phosphate, and 0.02% magnesium sulphate. Addition of 4% inoculum brought the final volume to 260 ml. All fermentations were carried out at 33 ± 1° C.

Inocula prepared in flasks on a shaker started the fermentation more rapidly than those prepared in tubes without agitation (34). Although this effect is helpful in the precision control of pH, in that it allows earlier supervision and necessary adjustment, complete fermentation times and diol yields remain unchanged (4). Aliquots of a sterile stock solution (15 ml. at pH 6.9 to 7.0) containing 1% sucrose and 0.5% yeast extract, inoculated from a 48 hr. agar slant and incubated in 50 ml. Erlenmeyer flasks at 30° C. on a shaker for 16 to 18 hr., gave uniformly good results, and shortened the lag period to two to three hours. The inoculum was examined microscopically for purity and for uniformity before addition to the medium. At the end of each fermentation the maintenance of purity in the culture was established by plating and by the examination of Gram-stained smears.

Procedures in the use of the pH monitor have already been described (5, 6, 33). Supplementary techniques were developed during this investigation to overcome troublesome variations in electrode potential, which sometimes appeared immediately after sterilization of the electrodes by irradiation at λ 2537 in air, and occasionally also during the fermentation. These variations were traced to three main sources: (i) deterioration of the electrode glass, (ii) effects of drying on the bulbs, and (iii) imperfect lead contacts.

Much of the success in the precision control of pH depends on the care given to the glass electrodes. Deterioration begins with use, and the age of a glass electrode may be defined as the length of time it has been in contact with solutions (21). Normal deterioration is probably caused by the escape of sodium or lithium ions from the superficial film. With average care this process limits the useful period for a high-ohmic type (100 to 150 megohms), such as is used with the monitor, to one to two years at 25° C. This period may be lengthened as much as 30% by storage in the proper medium (21). The rate of deterioration approximately doubles for each rise in temperature of 10° C. Sterilization of the glass electrodes by irradiation in air at λ 2537 superimposes on normal aging a more rapid deterioration caused by air drying at an elevated temperature (8). This was eliminated by immersing the bulbs in water contained in dishes of Vycor 791. Electrodes that had become prematurely unusable were readily restored to give precision control by immersing the bulbs for 30 sec. in 10% hydrofluoric acid, followed by several hours in distilled water.

The form and mounting of the electrodes are of critical importance in maintaining cultural purity, and also in the accurate reporting of changes in e.m.f. correlated with pH changes in the flasks. Electrodes with long (7 in.) glass salt-bridge tubes (e.g., Leeds and Northrup 1199-32) may be sealed through reduced 24/40 standard taper joints with high-melting paraffin and polyethylene cement, in a manner that permits sterilization without effecting

any change in the calibration of the bulbs (46). In order to adapt this preferred electrode to a rotating system (6, 33) changes were made in the lead contacts.* These changes not only freed the circuit from fortuitous variations in potential due to faulty contacts, but increased the percentage of successfully controlled fermentations by eliminating losses due to occasional breakages of the leads.

The methods of analysis for 2,3-butanediol, acetoin, ethanol, carbon dioxide, and hydrogen have been previously described (31, 41). Organic acids were determined by partition chromatography (32), and carbon assimilated by wet combustion (33, 45). Residual invert sugar was estimated by the Underkofler semimicro modification of the Shaffer–Somogyi method, standardized with hydrolyzed sucrose (13).

Results

Selection of the most favorable of the common soluble alkalis and of the best strain of *B. polymyxa* preceded establishment of the optimal pH level and of the most suitable sucrose concentration under aerobic and anaerobic conditions. Carbon balances for the anaerobic fermentation of 5% sucrose at pH 7.2 by strain C3(2), in which sodium, potassium, and ammonium hydroxides were used to maintain pH are given in Table I. Use of either sodium or potassium hydroxide in place of ammonium hydroxide retards the fermentation rate so that the period for complete dissimilation is increased more than five times. The yields of ethanol and acetoin are normal for an anaerobic fermentation. The low diol yields are explained by the well known inactivation of the acetoin enzyme system near pH 7.0 (28). Differences between the alkalis become accentuated at a pH as high as 7.2, since much larger amounts must be added for neutralization at this comparatively high pH level. It is difficult to explain the unusually high percentages (169 to 181 mM. per 100 mM. of invert sugar fermented) appearing as carbon assimilated in Table I. These are corrected values and they point to the action of factors other than vigorous growth and the absence of lysis. They may be correlated with polymer formation during carbohydrate degradation.

The response of three different strains to standardized anaerobic conditions in a 4.8% sucrose medium at pH 7.2 is shown in Table II. Strains C3(2) and UA206 display greater sensitivity to continued neutralization of the medium than C42(3)E13. The enzyme system in strain C42(3)E13 responsible for acetoin production apparently becomes inactive only at a higher pH. Compared with normal yields, ethanol production is most markedly increased and diol yield decreased with strain C3(2). The reduced carbon dioxide

*The lead wire from the Standard 1199–32 electrode is removed, the top of the aluminum cap threaded for a ¼ in. stainless steel plug 1½ in. long, and bearing upper and lower pins (10 mm. and 5 mm. long respectively) turned from the body of the plug. The aluminum cap is partially filled with mercury, the plug inserted, and a silver-plated beryllium-copper spring clip is attached to the upper pin. A 10 in. double (loop) phosphor-bronze dial cord is soldered to the clip and to the cable leads.

TABLE I

ANAEROBIC DISSIMILATION OF 5% SUCROSE BY STRAIN C3(2) AT pH 7.2 CONTROLLED BY SODIUM, POTASSIUM, AND AMMONIUM HYDROXIDES

Product	Millimoles per 100 mM invert sugar fermented		
	NaOH	KOH	NH_4OH
2,3-Butanediol	9.0	12.3	11.5
Acetoin	1.2	1.1	3.1
Ethanol	73.5	70.6	73.2
Acetic acid	25.6	22.5	21.1
Formic acid	1.9	1.5	11.7
Succinic acid	0.7	0.5	0.8
Lactic acid	2.3	2.3	1.4
Carbon dioxide	195.3	180.2	150.3
Hydrogen	161.9	144.5	95.8
Carbon assimilated	169.4	169.9	180.7
CO_2 obs./calc.	0.98	0.90	0.75
H_2 obs./calc.	1.62	1.45	0.96
$\frac{\text{Acetoin + diol}}{\text{Ethanol}}$ (by wt.)	0.3	0.4	0.4
Carbon recovery, %	103.0	100.3	100.1
O/R Index	1.15	1.11	1.10
Fermentation time, hr	119	119	23
% invert sugar used	97.6	92.1	100
pH at beginning	7.20	7.20	7.20
pH at end	7.20	7.24	7.31

TABLE II

ANAEROBIC DISSIMILATION OF 1.8% SUCROSE AT pH 7.2 BY THREE STRAINS OF *Bacillus polymyxa*

Product	Millimoles per 100 mM invert sugar fermented		
	Strain C3(2)	Strain CA206	Strain C42(3)E13
2,3-Butanediol	18.7	24.1	43.2
Acetoin	6.4	5.4	5.4
Ethanol	82.7	58.6	54.9
Acetic acid	50.4	13.3	23.4
Formic acid	9.1	2.1	14.3
Succinic acid	1.3	0.1	1.9
Lactic acid	2.0	1.6	1.7
Carbon dioxide	162.5	185.8	162.1
Hydrogen	109.3	128.2	75.5
Carbon assimilated	43.4	40.7	44.1
CO_2 obs./calc.	0.81	0.93	0.81
H_2 obs./calc.	1.00	1.28	0.75
$\frac{\text{Acetoin + diol}}{\text{Ethanol}}$ (by wt.)	0.6	1.0	1.7
Carbon recovery	100.0	93.6	98.2
O/R Index	0.96	1.12	1.03
Fermentation time, hr	22	31	19
% invert sugar used	99.8	99.6	99.2
pH at beginning	7.20	7.20	7.20
Final pH	7.20	7.34	7.43

formation (80 to 90% of theoretical) is correlated with an increase in the production of organic acids.

The apparent sensitivity of strain C3(2) to changing hydrogen ion concentration led to an investigation of its response over a range of pH levels (Table III). To summarize the results, there is a marked change in the chemical balance near pH 7. Diol and ethanol yields become almost normal below

TABLE III

ANAEROBIC DISSIMILATION OF 4.8% SUCROSE AT VARIOUS pH LEVELS BY STRAIN C3(2)

Product	Millimoles per 100 mM. invert sugar fermented					
	pH 5.2	pH 5.6	pH 6.0	pH 6.4	pH 6.8	pH 7.2
2,3-Butanediol	56.0	55.4	50.3	56.3	49.6	18.7
Acetoin	3.0	2.2	2.8	1.2	1.9	6.4
Ethanol	70.3	71.9	57.2	65.4	69.6	82.7
Acetic acid	0.9	1.1	1.3	7.3	19.0	50.4
Formic acid	0.4	0.4	0.5	0.3	0.6	9.1
Succinic acid	0.9	0.6	0.3	0.4	0.3	1.3
Lactic acid	1.0	0.7	1.4	1.5	0.7	2.0
Total organic acids	3 3	2.9	3.6	9.6	20.7	64.0
Carbon dioxide	201.8	181.8	203.8	197.3	193.5	162.5
Hydrogen	102.4	84.7	113.8	102.4	109.0	109.3
Carbon assimilated	27.5	27.1	25.1	29.7	8.8	43.4
CO_2 obs./calc.	1.01	0.91	1.02	0.99	0.97	0.81
H_2 obs./calc.	1.02	0.85	1.14	1.02	1.09	1.09
$\frac{\text{Acetoin + diol}}{\text{Ethanol}}$ (by wt.)	1.6	1.6	1.8	1.7	1.4	0.6
Carbon recovery	102.6	98.5	94.2	101.6	98.4	100.0
O/R Index	0.97	0.91	1.06	0.98	0.98	0.96
Fermentation time, hr.	71	71	29	27	26	22
% invert sugar used	98.4	95.2	91.3	97.2	97.6	99.8
pH at beginning	5.20	5.60	6.00	6.10	6.80	7.20
Final pH	5.27	—	6.19	6 52	7.01	7.20

pH 6.8 while above this level they are suppressed and acids accumulate. This confirms the results obtained by Neish and Ledingham (33) and an observation by Adams and Leslie (2) on pH controlled fermentations of whole wheat mashes by strain C3(2). Production of total and individual acids decreases steadily as the pH falls to 5.6. The marked increase in acid production above pH 6.8 is correlated with a decrease in carbon dioxide formation. Over the entire range from pH 5.2 to 6.8 the production of carbon dioxide remains close to the theoretical. From pH 5.6 to 6.0 there is a conspicuous drop in the time for 95% dissimilation, followed by a slow steady decline as the pH increases to 7.2. Neish and Ledingham (33) using strain C2(1) found the shortest fermentation period to occur at pH values of 6.2 to 6.8. Variations in the percentages of total carbon assimilated are probably associated with the varying degrees of autolysis that occur in an aging culture (23).

For comparison the effects of a range of pH levels on product yields from C42(3)E13 in 4.8% sucrose under similar conditions are shown in Table IV. The general observations apply to the data from both strains. Total yields of diol plus acetoin are somewhat higher at a given pH than with C3(2), although the diol yields themselves are lower. Stahly and Werkman (40) have shown that diol–acetoin ratios are correlated with changes in the oxidation–reduction potential.

TABLE IV

EFFECTS OF pH LEVELS ON PRODUCT YIELDS FROM STRAIN C42(3)E13 IN 4.8% SUCROSE UNDER DEOXYGENATED NITROGEN

Product	Millimoles per 100 mM. invert sugar used			
	pH 6.0	pH 6.4	pH 6.8	pH 7.2
2,3-Butanediol	52.0	53.5	50.4	43.2
Acetoin	4.2	4.9	4.2	5.4
Ethanol	57.6	58.2	56.8	54.9
Acetic acid	4.4	12.2	12.0	23.4
Formic acid	0.7	1.1	0.7	14.3
Succinic acid	0.4	0.4	0.7	1.9
Lactic acid	2.0	2.7	1.6	1.7
Total organic acids	7.8	16.8	15.5	42.2
Carbon dioxide	189.7	176.0	193.5	162.1
Hydrogen	71.8	66.3	88.8	75.5
Carbon assimilated	62.2	44.4	23.8	44.1
CO_2 obs./calc.	0.95	0.88	0.97	0.81
H_2 obs./calc.	0.62	0.66	0.89	0.75
$\frac{\text{Acetoin + diol}}{\text{Ethanol}}$ (by wt.)	1.9	2.0	1.9	1.7
Carbon recovery	101.8	101.4	97.4	98.2
O/R Index	1.08	1.00	1.06	1.03
Fermentation time, hr.	48*	48*	48*	19
% invert sugar used	97.3	97.7	98.3	99.2
pH at beginning	6.00	6.40	6.80	7.20
Final pH	6.12	6.46	6.84	7.43

Not true fermentation time.

Complete balances for the anaerobic dissimilation of sucrose in varying concentrations by strain C42(3)E13 at pH 6.2 are given in Table V. Diol yields increase and ethanol yields decrease steadily with increasing sucrose concentration. Up to 8% of sucrose, increases in diol yield are accompanied by decreasing accumulations of acetic acid (28, 35) and slight increases in the production of lactic acid. This is confirmation of the data presented by Mickelson and Werkman (28) and by Reynolds and Werkman (35). The total organic acids produced per 100 mM. of invert sugar fermented decreases at first rapidly and then more slowly with increasing sucrose concentrations. (to 8%). Moreover there is a general but irregular increase in fermentation time as the percentage of sucrose in the medium increases (*vide infra*). The most efficient conversion to diol occurs in media containing about 8% sucrose,

TABLE V

PRODUCT YIELD VS. SUCROSE CONCENTRATION USING STRAIN C42(3)E13 AT pH 6.2 UNDER NITROGEN

Product	Millimoles per 100 mM. invert sugar used				
	4% sucrose	5% sucrose	6% sucrose	8% sucrose	10% sucrose
2,3-Butanediol	54.7	54.8	59.7	65.2	71.2
Acetoin	4.4	3.7	0.9	2.4	3.0
Ethanol	66.7	66.2	64.6	60.6	40.7
Acetic acid	14.3	8.9	3.5	1.9	7.4
Formic acid	0.6	0	0.2	0.2	0.3
Succinic acid	0.2	0.3	0.1	0.2	0.2
Lactic acid	1.9	1.7	3.1	3.5	4.2
Total organic acids	17.0	10.9	6.9	5.8	12.1
Carbon dioxide	218	199	175	186	170
Hydrogen	88	86	63.7	64.5	68.3
Carbon assimilated			6.0		16.5
CO_2 obs./calc.	1.09	1.00	0.87	0.93	0.85
H_2 obs./calc.	0.88	0.86	0.64	0.65	0.68
$\frac{\text{Acetoin + diol}}{\text{Ethanol}}$ (by wt.)	1.6	1.7	1.8	2.2	3.6
Carbon recovery, %	103.9	98.4	94.9	98.9	99.0
O/R Index	1.11	1.02	0.94	0.96	0.92
Fermentation time, hr.	25	29	23	30	71
% invert sugar used	86.3	95.7	95.0	99.2	94.4
pH at beginning	6.20	6.20	6.20	6.20	6.20
Final pH	6.21	6.25	6.30	6.21	6.23

in which 99% of the sugar is dissimilated in 30 hr., producing 65 mM. of diol per 100 mM. of invert sugar fermented.

Reports by various authors indicate that the optimal sucrose concentration for diol production varies widely with the precise conditions under which the fermentation takes place. Fulmer, Christensen, and Kendall (12) found an optimal initial sucrose concentration for *Aerobacter* of 8%, while Freeman reported a maximum diol yield (87.4% of theoretical) with an initial sucrose concentration of 15% (11). In the former investigation 20 days was required to complete the fermentation, while in the latter complete sucrose conversion took place in 35 hr.

For comparison of the aerobic and anaerobic dissimilations of sucrose, a similar series using strain C42(3)E13 was performed using air in place of nitrogen. Under these conditions dissimilation is slower, and at concentrations of 8 and 10% is incomplete even after 148 hr. (Table VI). Total yields of diol plus acetoin are considerably augmented, and remain fairly constant at about 80 mM. per 100 mM. of sucrose fermented. Ethanol yields show the conspicuous depression known to accompany aeration (1, 37). The large increase in the diol-ethanol ratio, which reaches a maximum at 10%, is thus explained. In contrast to their formation under nitrogen, total organic acids

TABLE VI

AEROBIC DISSIMILATION OF SUCROSE IN VARYING CONCENTRATIONS AT pH 6.2 BY STRAIN C42(3)E13

Product	Millimoles per 100 mM invert sugar used				
	4% sucrose	5% sucrose	6% sucrose	8% sucrose	10% sucrose
2,3-Butanediol	47.2	37.8	58.0	47.8	60.4
Acetoin	34.6	37.6	24.3	31.9	20.8
Acetoin + diol	81.8	75.4	82.3	79.7	81.2
Ethanol	11.6	23.7	20.2	17.6	13.8
Acetic acid	0.6	1.5	8.2	5.3	4.5
Formic acid	0.3	0.6	0.2	0	0
Succinic acid	0.2	0.2	0	0.2	0.2
Lactic acid	0.3	3.7	10.5	9.3	13.7
Total organic acids	1.5	9.0	18.9	14.8	18.4
Carbon dioxide	244	210	173	197	184
Hydrogen	1.0	2.0	1.0	1.0	0.8
CO_2 obs./calc.	1.22	1.05	0.86	0.98	0.92
H_2 obs./calc.	0.01	0.02	0.01	0.01	0.08
$\frac{\text{Acetoin + diol}}{\text{Ethanol}}$ (by wt.)	8.0	6.2	7.9	8.7	11.4
Carbon recovery, %	99.8	96.7	98.4	98.4	98.0
Fermentation time, hr.	59	104	71	148	148
% invert sugar used	98.8	89.5	96.5	83.4	78.5
pH at beginning	6.20	6.20	6.20	6.20	6.20
Final pH	6.31	6.21	6.21	6.20	6.27

increase under air with increasing sucrose concentration from 4 to 6%, and remain relatively constant at higher concentrations. Dissimilation of 6% sucrose becomes 98% complete in 71 hr., and produces 82% by weight of theoretical diol plus acetoin. The conspicuous and irregular differences in diol yield, along with the relative constancy of total diol plus acetoin, is further evidence of fluctuations in *Eh* (40). These data confirm the conclusion of Adams, based on the fermentation of wheat mashes under aerobic and anaerobic conditions (1).

The physical and chemical factors influencing each fermentation had been standardized as carefully as possible, but marked fluctuations are still apparent in carbon dioxide production and in ethanol and acid yields. These fluctuations have been ascribed to the inherent variability of the organism (2), the basis of part of this variability may reside in trace-element sensitivity (29).

The examples of irregular fermentation times provided in Tables V and VI are often observed in studies with *Bacillus polymyxa*. These apparently fortuitous variations are correlated with cessations of acid production recorded by the monitor (6). The duration of such 'rest periods' varied from several to many hours. Recovery invariably followed and dissimilation proceeded. Microscopic examination during a quiescent period revealed no visible abnor-

malities in the organism. Disappearance of a necessary growth factor and its subsequent resynthesis by the organism offers one of a number of possible explanations.

Discussion

The effects of pH on fermentation efficiency are slight from pH 6.0 to 6.4, although they become accentuated above and below this range (Tables III and IV). Increased fermentation times accompany reduction of the pH much below 6.0. Above pH 6.0 the increased production of total organic acids by both C3(2) and C42(3)E13 is correlated with a general decrease in carbon dioxide production. Moreover, diol yields begin to show a decrease above pH 6.4 and the increased acid production necessitates increased additions of alkali. Favorable yield of diol, low acid production, low alkali utilization, and favorable fermentation rate point to a maximum efficiency in the vicinity of pH 6.2. This corresponds closely with the recommended optimum of 6.0 in whole wheat mashes (2) and of pH 6.2 in glucose dissimilation (33). It also coincides with the optimum pH of 6.2 selected by Kendall for *Aerobacter* spp. (20) and this observation is supported by the evidence for a critical pH level of 6.3 for *A. indologenes*. It was demonstrated by Mickelson and Werkman that acetic acid is condensed to acetoin below pH 6.3, whereas above this level it accumulated as the free acid (28). If choice of the optimum pH is based on glycol yield, the data of Freeman point to an optimum from pH 5.0 to 5.5 for *A. aerogenes* 199. The initial rate of sucrose conversion was 25 to 30% greater at pH 6.0 to 6.5 than at 5.0 to 5.5, but the final glycol yield was 22% higher over the lower range (11). Analyses of end products in the present investigation provided no evidence that measurable changes in yields follow variations of $\pm$ 0.1 pH units. Statistical analysis of the results from a series of closely controlled runs would be necessary to determine the effects of such minor deviations.

The final pH values in Tables I to VI are relative. They were obtained by calibrating the monitor at a temperature of 33° $\pm$ 1° C. with a buffer standardized on the Sørensen scale at 18° C.* (7) and retaining the buffer to recalibrate a pH meter at room temperature at the end of the fermentation. The pH of the fermented liquor was *always* higher than that of the original setting, often by as much as one or more units. No critical analysis of the factors that may be responsible for this swing to alkalinity at the end of the fermentation period has been made. The difference in number of scale units between the original potentiometer setting and the final setting at re-balance divided by 295 gave the difference, x, in pH units from the original setting. The divisor (295) is based on a value of 0.059 v. per pH unit, and an exact calibration of 5.0 scale divisions per millivolt. Addition of the x value to the pH of the buffer and comparison of this total with the reading of the pH meter gave the 'final pH' values recorded in Tables I to VI. For 20 of the 23 fermentations the deviation is positive (average = + 0.08), i.e., the calcu-

**Clark and Lubs $NaOH.KH_2PO_4$ mixtures.*

lated pH is below that of the fermented liquor. This consistently positive deviation points to inaccuracy in one or more of the measurements. Differences between the standardization temperature of the buffer and that at which it is used in calibrating the monitor and the pH meter, changes in the liquid junction potential, disbalance in the electronic control circuits with resulting inequalities in calibration at different points on the scale, use of the RT/F factor at 25° C. (i.e., 8° C. below the fermentation temperature), and changes in electrode e.m.f. during the period of measurement are some of the factors that may have contributed to the positive deviation. An evaluation of these factors will be made in a subsequent study.

The adverse effects of sodium and potassium hydroxides shown in Table I may be correlated with changes in cell permeability induced by excessive addition of unbalanced sodium or potassium ion. The marked acceleration in fermentation rate with the addition of ammonium hydroxide may be linked with beneficial effects on nitrogen metabolism. Insufficient evidence is available to allow evaluation of these two separate effects of ammonia. Freeman (11) has noted that fermentation rates and diol formation by *Aerobacter aerogenes* were lower in media controlled by stepwise addition of sodium hydroxide than in the presence of calcium carbonate. The difference was attributed to the unavoidable width of the pH steps between successive additions of alkali. Although wide fluctuations in pH doubtless have considerable influence, the toxicity of excess sodium or potassium ion may be partly responsible for the low fermentation rates and diol yields. From a comparison of *B. polymyxa* fermentations of whole wheat mashes (*a*) buffered by calcium carbonate and (*b*) controlled by additions of ammonia, Adams and Leslie (2) selected the latter as preferable because of its inherent sterility, range of control, ease of addition in either the liquid or the gaseous state, and lower cost. To these advantages may be added a supply of available nitrogen and acceleration of the fermentation rate with automatic pH control.

All the products reported in the carbon balances have been characterized for this fermentation (9). Other compounds, e.g., malic acid and acetone, are known to occur in media fermented by certain strains of *B. polymyxa* (9, 36) and some evidence for the presence of small amounts of these substances was obtained. The formation of traces of acetone was revealed in about half of the fermentations by the oxime method (15) after applying corrections for acetoin (31). Traces of malic acid were disclosed by filter paper chromatography, and the application of Shupe's method (38) showed the possible presence of glycerol. These compounds were not present in amounts sufficient to affect the carbon balances and they have been omitted from the tables.

There is still no general agreement as to the mechanism by which acetoin arises in the degradation of carbohydrates by bacteria, although there is evidence that pyruvic acid and acetaldehyde may be the immediate precursors. (14, 39). The mode of ethanol formation is also obscure. A common

explanation of the effect of aerobic conditions on this fermentation has been that gaseous oxygen acts as a hydrogen acceptor, decreasing the reduction of acetaldehyde to ethanol and favoring its condensation to acetoin (1, 3). Rose pointed out the irrelevancy of this assumption (37) and Gale has recently suggested that *coli-aerogenes* organisms may produce ethanol directly from dihydroxyacetone phosphate (13). Most of the investigational evidence for this hypothesis has been obtained from members of the *coli-aerogenes* group and additional information must be collected before its extension to the carbohydrate metabolism of *B. polymyxa*.

Acknowledgments

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ON THE USE OF CRYSTAL CONTROLLED SYNCHRONOUS MOTORS FOR THE ACCURATE MEASUREMENT OF TIME[1]

By V. E. Hollinsworth

Abstract

Making use of the quartz frequency standard of the Dominion Observatory crystal clock an electronic frequency converter has been constructed that transforms the 50,000 cycle output of the crystal to a frequency of 60 cycles. Suitable amplification makes possible sufficient power for operating several standard 60 cycle motors and these are being used to drive printing and drum chronographs and for the operation of other types of recorders.

Introduction

There are many applications in scientific work for small synchronous motors capable of constant speeds of rotation. However, when such motors are operated from a commercial alternating current line, variations in frequency with resulting variations in motor speed often result in unsatisfactory performance. Particularly is this true in observatories and institutions concerned with the precise measurement and recording of time. For this reason a project was undertaken at the Dominion Observatory to develop a means of operating synchronous motors with a constancy of rotational speed corresponding to the performance of the best clocks. If accuracy of this order could be obtained, such motors could be used with suitable electrical contacts to operate clock dials, for use as interval timers or as drives for chronograph drums, printing chronographs, and other types of time recorders.

The principle adopted for the control of motor speed was to make use of the vibrational qualities of quartz crystals to provide an alternating current of constant frequency, and then by the use of frequency dividers followed by a stage of frequency multiplication and suitable amplification to produce 60 cycle power sufficient to operate a number of small synchronous motors.

Quartz has long been known to have piezoelectric properties (1), that is, it will transform a mechanical strain into an electrical charge and vice versa. A suitably cut quartz wafer (6) or bar may be sandwiched between two electrodes and made to vibrate mechanically at its resonant frequency by the application of alternating electrical pulses to the electrodes, and if the timing of the pulses is correct, the vibrations of the quartz will be maintained. The crystal may be coupled to an electrical circuit and in effect made to substitute for a coil and condenser resonant circuit (9). As the crystal will not vibrate at frequencies other than that at which it is resonant, the circuit that it controls will function only at that particular frequency.

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If the temperature of the crystal is controlled within sufficiently narrow limits, in a suitable thermostat, the variations in the natural frequency of the crystal will be extremely small, so small in fact that such crystals have now become among the world's best timekeepers (2). Crystal controlled clocks have largely supplanted the pendulum type as master timekeepers in most observatories (3, 4, 5). Quartz crystals of suitable physical dimensions are also used to accurately maintain the broadcast frequencies of all radio stations.

The problem of crystal control of synchronous motors thus becomes that of obtaining a low frequency crystal and subdividing its natural period of vibration in steps, having a ratio of not greater than 10 to 1, until the desired output frequency is obtained. Precision quartz plates are usually cut to have a natural frequency of either 50 or 100 kc. (6). The first frequency divider would reduce this to 10 kc., the second to 1 kc., the third to 100 cycles, the fourth to 10 cycles, and this may then be multiplied six times to give 60 cycle current. As very little power is available from these frequency changing circuits, a heavy duty power amplifier as the final stage is required to supply sufficient voltage and current for the operation of a number of motors.

Let us now consider the practical construction of an Electronic Frequency Converter to operate on the principle outlined above. At the Dominion Observatory the availability of a crystal clock (General Radio Frequency Standard) with a 50 kc. quartz crystal and an output frequency of 1000 cycles provided an excellent base on which to build. It was necessary to construct only three units to convert this 1000 cycles to 60 cycles (7, 8) plus a power amplifier to deliver the desired voltage and current for motor operation.

The first unit reduced the frequency to 100 cycles, the second to 10 cycles, and the third increased it to 60 cycles. Other frequencies might have been chosen, viz., 1000 to 3000 cycles, 3000 to 300 cycles, and 300 to 60 cycles, but it was considered advantageous to have both 100 cycle and 10 cycle outputs available for other purposes.

An examination of the circuit diagram of the first unit, Fig. 1, will serve to illustrate the principles involved. The first tube is merely an amplifier to isolate the frequency determining circuit from the input line. The second and third tubes, with their associated condensers and resistors, generate recurring pulses at the rate of 100 per sec., since the values of condensers and resistors that will produce this frequency were selected.

The recurring feature is procured by feeding back some of the output voltage from the third tube to the grid of the second tube; this causes the circuit to oscillate. An adjustable resistor makes it possible to set the frequency of oscillation at the desired value. In practice this setting is just under 100 cycles so that the oscillator is just about ready to produce a pulse when every tenth pulse of the 1000 cycle control frequency arrives and initiates

it This, then, is the method of control and may be carried on in the two following units to supply a final frequency of 60 cycles controlled by the 1000 cycle supply which, in turn, through intermediate stages is controlled by the 50 kc crystal

100 CYCLE FREQ DIVIDER
TYPE 6J5G TUBES

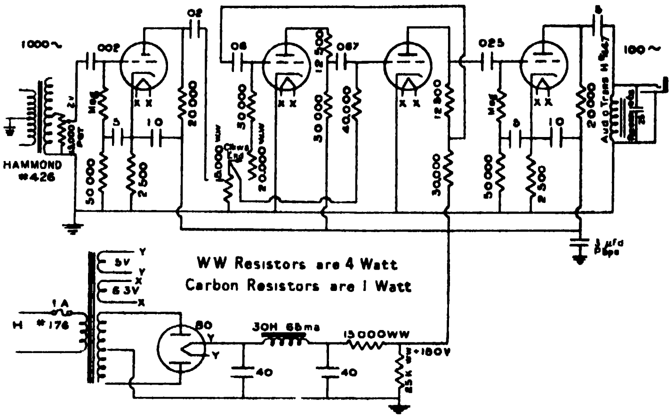


FIG 1

The fourth tube in the circuit is an isolating amplifier to prevent succeeding stages from interfering with the frequency determining network, and is also the place selected to install a resonant circuit, i e, a transformer tuned to

10 CYCLE FREQ DIVIDER
TYPE 6J5G TUBES

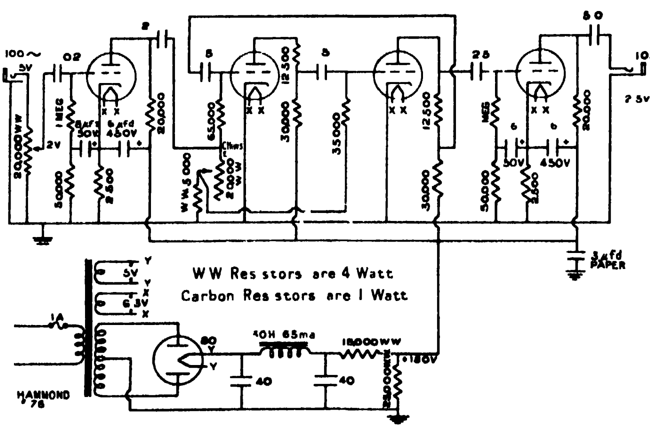


FIG 2

100 cycles by a condenser, to produce sine wave form from the "sawtooth" type generated by the oscillator. If this is not done the succeeding 10 cycle stage is likely to be triggered by one of several spurious peaks appearing on the ragged untuned wave.

The above description of the operation of the 100 cycle frequency divider applies generally to both the 10 cycle unit, Fig. 2, and the 60 cycle unit, Fig. 3. However, a few points in the 60 cycle unit warrant further description. As

60 CYCLE FREQ. MULTIPLIER
TYPE 6J5G TUBES

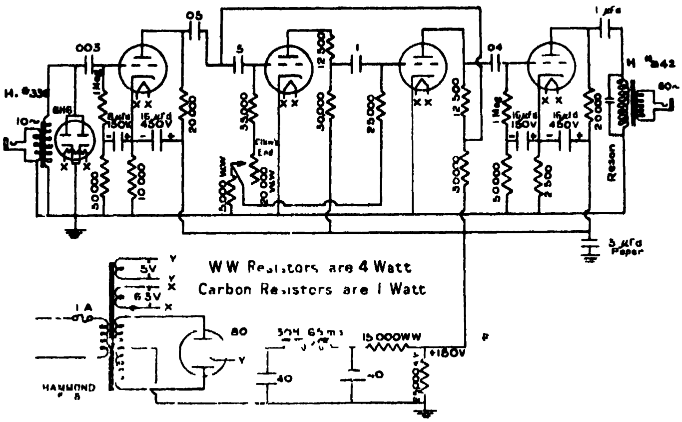


Fig. 3.

the 10 cycle pulse is normally much broader than a 60 cycle pulse, some means had to be found of narrowing the wave form in order that a definite influence, or triggering action, should be exerted on a single wave, i.e., every

60 CYCLE POWER AMPLIFIER

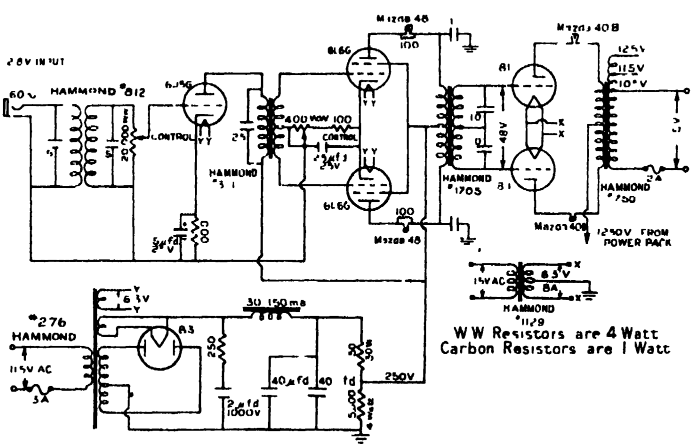


Fig. 1.

sixth wave of the 60 cycle unit, without disturbing the fifth or seventh waves. It was thought that this could be accomplished by using a high driving voltage on the grid of the first tube in the 60 cycle unit, and biasing the grid sufficiently

negative so that only the peaks of the positive swing would be effective in changing the plate current of this tube. As the peak is much narrower than the whole wave this method would appear to be satisfactory. This was found to be so when the input circuit, Fig. 3, was constructed as shown. An audio transformer with a 1 : 3 turn ratio was used to boost the voltage and a 10,000 ohm cathode resistor supplied sufficient bias. The unwanted negative portion of the voltage wave was shorted out by suitably connecting a half wave rectifier across the transformer secondary.

In other respects the 60 cycle unit is similar to the 100 cycle unit described above.

AMPLIFIER POWER SUPPLY

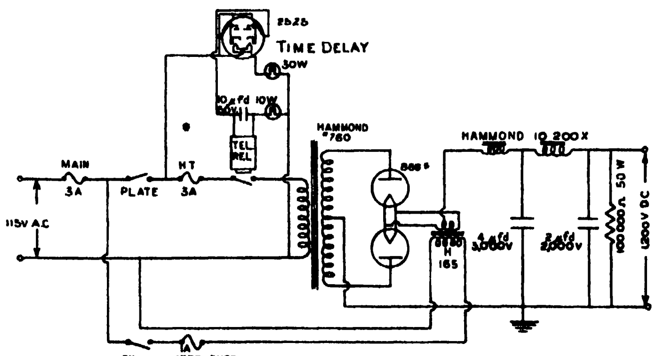


FIG. 5

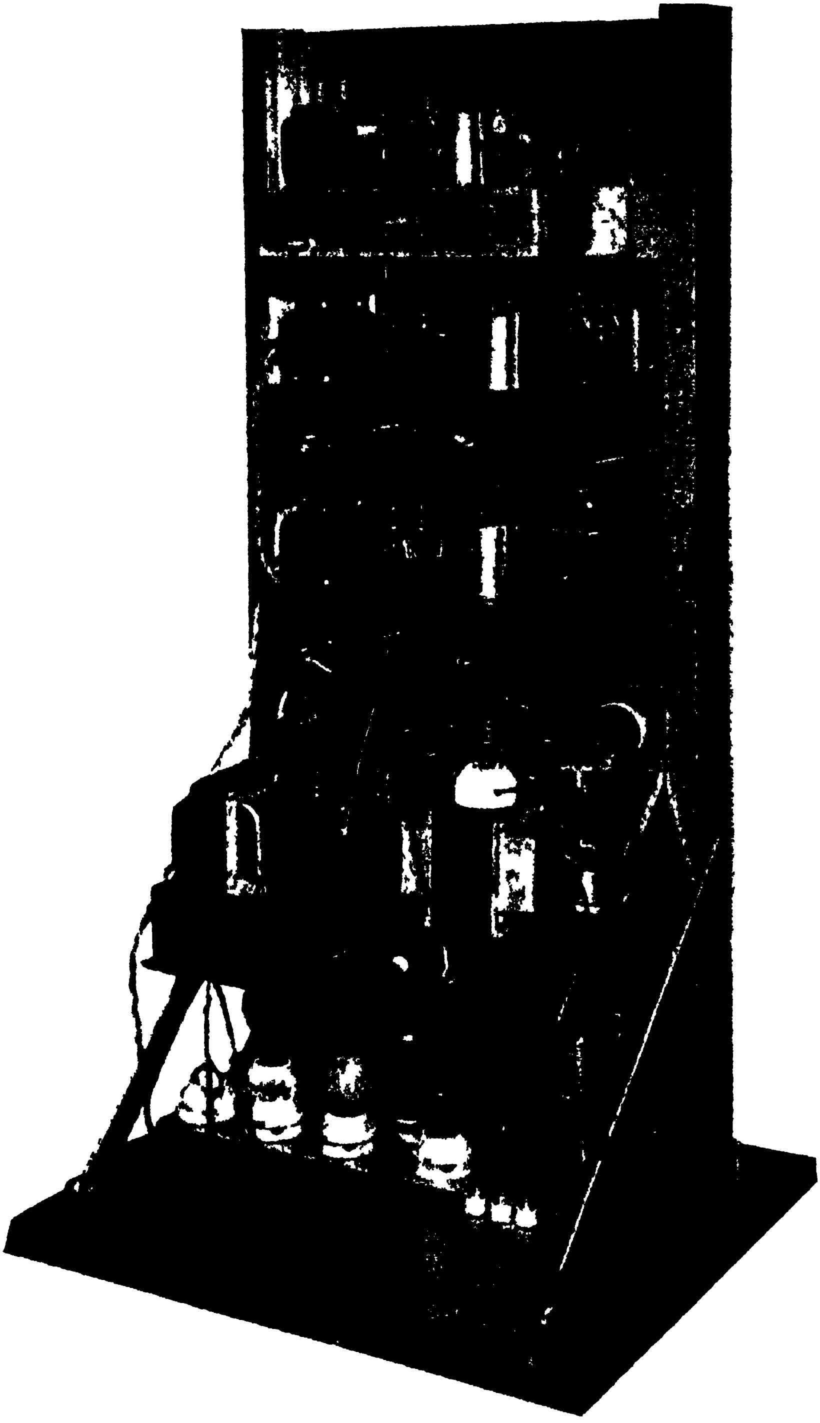
A heavy duty amplifier, Fig. 4, was constructed to build up the output of the 60 cycle unit to supply sufficient power both for the operation of synchronous motors and for providing stability so that the addition or removal of several motors would not seriously alter the voltage. The one constructed for use at the Dominion Observatory will deliver up to 150 w. at 115 v. with sine wave form. This power is sufficient to operate quite a number of small motors drawing from 2 to 10 w. each.

Type 811 tubes were used, as these are capable of delivering the required power and are available cheaply as war surplus.

A conventional class "B" circuit was employed, using push-pull 6L6 tubes as drivers, which were, in turn, controlled by a single 6J5 input tube. The input circuit was resonated at 60 cycles to ensure that the input, and hence the output, would be of sine wave form

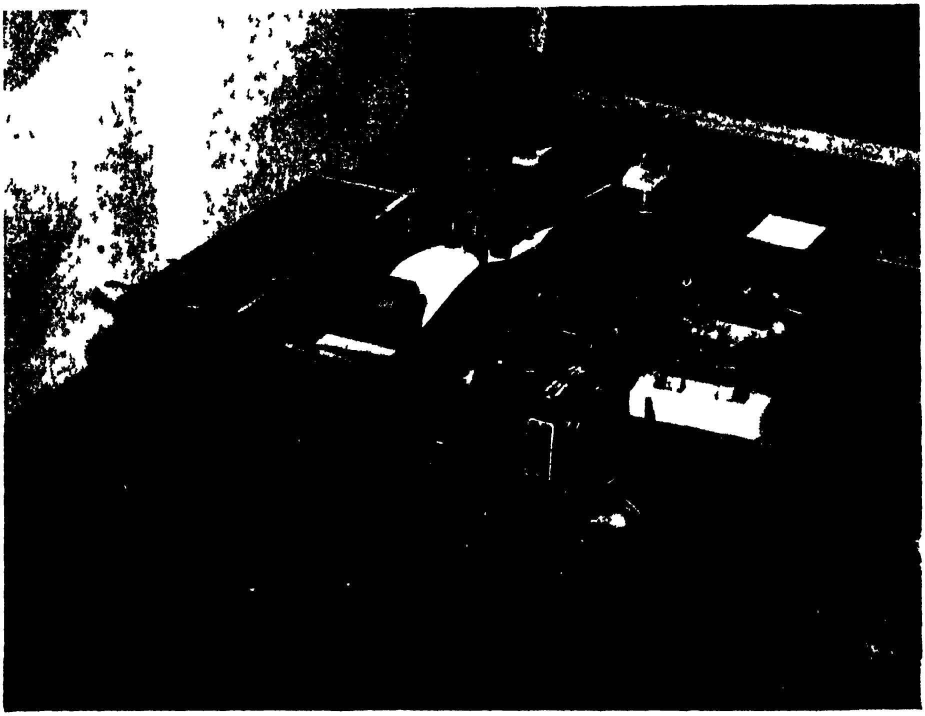
A heavy duty power supply, Fig. 5, was constructed on a separate chassis to supply the plate voltage for the Type 811 tubes. These require 1200 v. at 200 ma. for full output, so components capable of delivering this power were used. As our present loading of 40 w. represents less than 30% of full load capacity, the equipment runs cool and has a large factor of safety. As

PLATE I



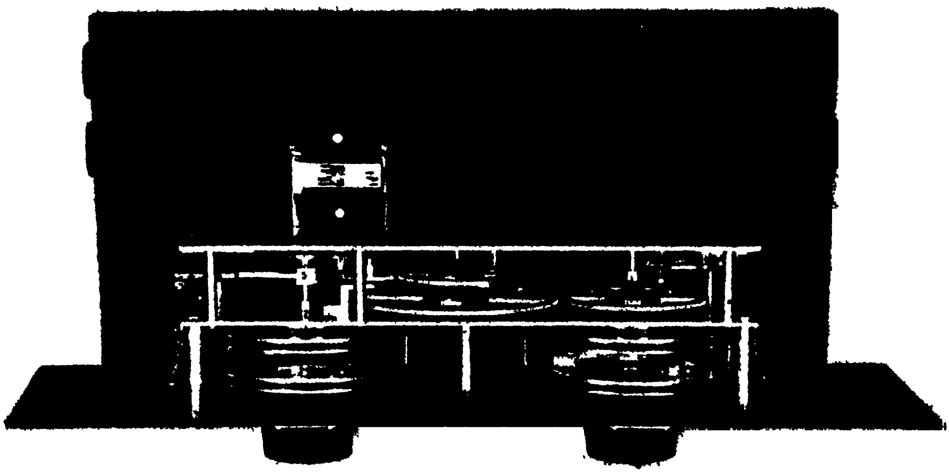
Rear view of Dominion Observatory electronic frequency converter, etc.

PLATE II



Showing the application of a synchronous motor to drive the type wheels of a printing chronograph

PLATE III



A synchronous motor driven time converter to derive sidereal time from mean time

many as 10 motors could be operated continuously and still leave a satisfactory operating margin.

Good filtering of the rectified a. c. is required to avoid locking-in of the 60 cycle controlled frequency with the a-c. line frequency.

All components used throughout were underrated so that the resulting large safety factor would minimize break downs.

Many uses are being found for this crystal controlled source of power. Both high and low speed recording chronograph drums are being driven by synchronous motors. The rotating type wheels of the printing chronograph, Plate II, are also being operated this way with considerable improvement over the governor method. Small synchronous clock motors equipped with contacts are being used to give seconds impulses and a gear train Time Converter, Plate III, has been constructed to produce sidereal time from mean time when synchronously driven.

To measure the accuracy, as a timekeeper, of a motor controlled by the above power supply, a second's contact was actuated by the rotor of a Bodine motor (60 r.p.m.). Comparisons were made with the original crystal clock, and the variation between the two was of the order $\pm 1 \times 10^{-3}$ sec. This was the limit of measurement and very likely the variation is considerably less than this quantity.

All units are rack mounted as illustrated on Plate I. This affords economy of space and enhances the appearance.

Early causes of "pull out" have been analyzed and corrected, and during the past year the operation of this equipment has been very satisfactory.

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FACTORS AFFECTING THE DETERMINATION OF MOISTURE IN HARD RED SPRING WHEAT BY COMMERCIAL ELECTRICAL METERS[1]

By A. E. Paull[2] and V. Martens[3]

Abstract

Statistical analysis of data obtained with eight commercial electrical moisture meters and 159 samples of Hard Red Spring wheat shows that variations in bushel weight and kernel weight have an effect on the moisture readings but variations in protein and ash content do not. An appreciable amount (from 10 to 30%) of the variation in the G.R.L., Steinlite, Marconi, and Mullard readings is attributable to variations in bushel weight alone; and in the Patterson and Tag–Dielectric readings to bushel weight and kernel weight jointly. The Tag–Heppenstall and Universal meters are not influenced appreciably by the factors investigated.

Introduction

A recent paper from this Laboratory (4) presented results of a comparative study of 10 electrical moisture meters based on observations on 159 samples of hard red spring wheat. All machines measured the electrical property of the samples, either resistance or capacitance, with good precision, but for some machines the correlation between the electrical property and moisture content was considerably better than for others. Electrical properties of a grain sample are dependent also on factors other than moisture content, and these additional factors have a greater influence with some meters than with others. The present paper shows that the average size and shape of the wheat kernels, as estimated by bushel weights or 1000-kernel weights, affect meter readings, but that the readings are not affected by the protein or ash content of the samples.

Materials and Methods

Data for eight meters, Tag–Heppenstall, Universal, Tag–Dielectric, G.R.L., Patterson, Steinlite, Mullard, and Marconi, have been examined. An earlier paper (4) described methods used for determining the moisture contents of 159 wheat samples by the split vacuum oven method and with the electrical meters. Other measurements were made by standard methods. Ranges for the series of samples were: moisture, 11.7 to 17.6%; bushel weight, 55 to 65 lb.; 1000-kernel weight, 17.8 to 35.1 gm.; protein content, 12.4 to 19.2%; and ash content, 1.27 to 1.98%. Levels of these properties were distributed randomly over the respective ranges.

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Paper No. 102 of the Grain Research Laboratory, Board of Grain Commissioners for Canada, Winnipeg, Manitoba, and No. 276 of the Associate Committee on Grain Research.
[2] *Biometrician.*
[3] *Senior Technician.*

Multiple regression methods were used to study the possible effects of these properties on meter estimates of moisture content, and tests of significance were applied to determine whether the effects observed were likely to have arisen other than by chance. Those factors for which a real effect was demonstrated were then examined to determine by how much the error of estimating moisture would be reduced if the effects of the factor were eliminated.

Results

Bushel weight exhibits an influence on moisture readings for all the meters tested, and kernel weight exhibits an influence on all except the Mullard, although in both cases the effects for the Tag–Heppenstall, Universal, and Tag–Dielectric meters are so small as to be of little practical importance. Neither protein nor ash content gives evidence of influencing the moisture readings of any of the meters.

TABLE I

STANDARD ERRORS OF ESTIMATE IN MOISTURE READING UNITS AFTER ADJUSTING FOR MOISTURE CONTENT, BUSHEL WEIGHT, AND KERNEL WEIGHT

	Total error of estimate of moisture	Errors of estimate after adjusting for:		
		Moisture and bushel weight	Moisture and kernel weight	Moisture, bushel weight and kernel weight
Tag–Heppenstall	0.23	0.23	0.22	0.21
Universal	0.27	0.27	0.26	0 25
Tag–Dielectric	0.34	0.34	0.33	0.31
G.R.L.	0.35	0.25	0.33	0.24
Patterson	0.39	0.38	0.39	0.34
Steinlite	0.41	0 30	0.38	0.30
Mullard	0.45	0.40	0.42	0.40
Marconi	0.53	0.39	0.50	0.38

A more detailed account of the relative effect of bushel weight and kernel weight is given in Table I. Standard errors of estimate are presented for the eight meters when no account is taken of kernel characteristics, and also when adjustments are made for bushel weight and kernel weight measurements both separately and jointly. For example, the entries for the G.R.L. meter show that, by the usual procedure, two-thirds of the moisture estimates given by the meter will lie within ±0.35 of their true value. If, however, over the same series of samples, allowance is made for the variations in bushel weight, then two-thirds of the estimates will lie within ±0.25 of their true values. Making allowance for kernel weight instead results in a standard error of ±0.33, while adjusting for both bushel weight and kernel weight results in a standard error of ±0.24. Generally, adjusting for bushel weight alone yields estimates at least as good as those obtained by adjusting for kernel weight alone; and except on the Mullard machine, adjusting for both factors

jointly results in significantly better estimates than adjusting for only one of these factors, although the improvement in this case is sufficiently large to be of practical importance only in the Patterson and Tag-Dielectric meters.

Discussion

No evidence was obtained that the nonaqueous constituents of the kernels affect electrical properties. Though the series of samples represented wide ranges of protein and ash contents, neither of these constituents, nor any that may be closely associated with them (e.g., starch), appear to have an appreciable effect on the resistance or capacitance of the wheat. Neitzert (5), who also gives an extensive review of European and American studies of moisture meters, shows a relation between specific resistance and ash content for three samples of flour. An increase of 1% in ash content appears to result in an increase of about 1% in the estimate of moisture. No similar relation was established in this laboratory for wheat, though there was some indication of a minor effect.

Among other factors that affect the estimates, temperature is of marked importance (1, 4), and this fact is taken into account by the manufacturers of all meters. Abnormal moisture distribution has been shown to have a marked effect on the electrical estimation of moisture content. Hartshorn and Mounfield (3) observed that artificially damped wheat tends to give unduly high readings. Abnormalities in the moisture distribution doubtless account also for the widely experienced difficulty in obtaining accurate meter estimates of moisture content in freshly harvested wheat and in wheat that has been rapidly dried.

There is a high correlation between bushel weight and kernel weight, so that it is difficult to conceive of the effects of these factors separately. Taken jointly, they may be considered as a good measure of kernel size and weight. It thus appears that these two properties affect moisture readings in all meters. Adjustments for bushel and kernel weights reduced the error of estimate least for the resistance type meters, Tag-Heppenstall and Universal, in which differences in size and shape of kernels are offset by partial crushing of the grain. The largest reductions occur in the Marconi, Steinlite, and G.R.L. meters.

Differences in size and shape of kernels can influence electrical readings in several ways. Variations in these properties result in variations in the closeness of packing in the dielectric type meters. This in turn yields differences in the grain/air ratio with resulting differences in the specific inductive capacity of the mixture. Yevstingneyev (6) dealt extensively with this matter in his study of measurement of the dielectric constant in flour. His paper also reviews earlier work dating back to 1894.

A further consequence of variations in kernel characteristics is the differences in weight, from sample to sample, when a fixed volume of grain is used; or

the differences in volume when a fixed weight of grain is used. For example, the Marconi meter employs a fixed volume of grain, so that it estimates essentially the moisture percentage by volume. Percentages by volume will differ from percentages by weight, over a series of samples, if there are differences in bushel weight. Accordingly, it was to be expected that the partial regression coefficient for bushel weight would be larger for the Marconi meter than for any of the others. A change of 1 lb. in bushel weight resulted in a change of 0.23% in the Marconi moisture reading; the next largest coefficient was 0.18% for the Steinlite meter, whereas the smallest coefficient for capacity type meters was 0.09% for the Tag-Dielectric.

In meters using a constant weight of grain, variations in size and shape of kernels create differences in the volume of the test sample. The load line of the condenser may thus vary from sample to sample, and resulting changes in end effect in the condenser will contribute to the error of estimate. This difficulty has been emphasized by Groves and King (2). It appears that it might be largely overcome by compression of a constant weight of grain to a constant volume.

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ESTIMATION OF LIPASE IN DAIRY PRODUCTS

I. AN EXTRACTION-TITRATION METHOD FOR THE ESTIMATION OF MILK LIPASE[1]

By L. M. Smith[2], D. J. Lubert[3], and H.R. Thornton[4]

Abstract

A procedure has been outlined for the estimation of milk lipase. The method is based on the titration of an ether extract of butyric acid derived from the enzymatic hydrolysis of tributyrin under standardized conditions. Some of the fundamental factors involved in the procedure have been discussed. It is suggested that modifications of the method may be used to study lipase activity in other dairy products and in cultures of micro-organisms.

Introduction

Early methods for the determination of milk lipase have been reviewed by Rice and Markley (5) and Hileman and Courtney (2) and will not be discussed in this paper. The presence of free fatty acids indicating lipase activity in dairy products may be detected by organoleptic means, lowered surface tension of milk, or titration against a standard alkali. The first two methods are susceptible to interfering factors and are not quantitative. The third method has been used by various investigators including Mattick and Kay (3). Peterson *et al.* (4) eliminated the time-consuming steam distillation required in the Mattick and Kay method. Dunkley (1) modified the Peterson *et al.* technique by using an ether extraction to avoid titrating the liberated butyric acid in the presence of milk salts, proteins, and the barbiturate buffer. The present paper deals with a further modification of the method suggested by Dunkley.

The Method

Reagents

Borate buffer: 6.23 gm. boric acid and 50 ml. N sodium hydroxide per liter of solution

Titration mixture: 50 ml. 0.1% alcoholic cresol red in 1 liter 95% alcohol and 1 liter distilled water. Adjust mixture to pH 7.4 with 0.05 N sodium hydroxide.

Tributyrin (Eastman)

Molar phosphoric acid

Ethyl ether

Standard 0.025 N sodium hydroxide.

[1] *Manuscript received July 26, 1949.*
Contribution from the Department of Dairying, University of Alberta, Edmonton, Alberta. The data contained herein were taken from theses submitted to the University of Alberta by the two senior authors in partial fulfillment of the requirements for the degree of Master of Science. The study was supported by a grant from the Committee on Agricultural Research Grants of the University of Alberta.
[2] *Lecturer in Dairying.*
[3] *Sessional Instructor in Dairying.*
[4] *Professor of Dairying.*

Procedure

The sample of milk to be tested is centrifuged and 2 ml. of the skim milk is pipetted into a test tube containing 5 ml. of the borate buffer. The mixture is adjusted, if necessary, to pH 8.8 using 0.1 N sodium hydroxide or 0.1 M phosphoric acid. The buffered milk is brought to 37° C. in a water bath at that temperature within four minutes, 0.6 ml. of tributyrin is added and emulsified by vigorous shaking of the stoppered tube for five seconds. The mixture is then returned to the water bath and left undisturbed during the reaction period.*

At the end of the reaction period (30 min. after the addition of tributyrin) 5 ml. of molar phosphoric acid is added to stop hydrolysis and the test tube is inverted twice before transferring to a 20° C. water bath. After five minutes the mixture is shaken vigorously with 10 ml. of ethyl ether for five seconds. The test tube is returned to the water bath for another five minutes to allow the ether layer to separate and then the rubber stopper is loosened. After a further three minutes a 5 ml. aliquot of the ether layer is pipetted into a 50 ml. beaker containing 10 ml. of the titration mixture.

The solution is titrated with standard 0.025 N sodium hydroxide to a faint orange color and the number of milliliters required is designated as the "Titer". The blank determination is made in a similar manner except that the reaction period is omitted. Hydrolysis of the tributyrin is considered to be proportional to the concentration of lipase and is expressed as the difference between the sample and the blank titers.

The blank determination is affected by the presence of any free butyric acid in the tributyrin as well as by the presence of any organic acids in the milk sample. The blank titers of fresh milks are quite constant for a particular lot of tributyrin. For routine analyses of such milks this blank value can be used as a standard correction and only one titration carried out for each sample. However, this is not possible when dealing with milks that have undergone lipolysis or bacterial decomposition. In these samples the free fatty acids or such organic acids as acetic and lactic increase the value of the blank.

Experimental Techniques

The above procedure was followed in principle in the experimental work on the fundamental factors involved in the method. Buffers other than the standard differed only in the sodium hydroxide concentration. To keep the total volume for extraction reasonably uniform, 3.5 ml. of 1.5 M phosphoric acid was used in some of the experiments. All pH values were determined with a Beckman glass electrode pH meter. The milk samples were obtained from the University of Alberta herd and were held at 4° C. for periods from 2 to 48 hr.

* *The biochemical literature frequently but erroneously refers to this as an incubation period. As a true incubation period is an integral part of this procedure when adapted to the estimation of bacterial lipases, the time during which hydrolysis is permitted will be spoken of herein as the reaction period.*

Experimental

Titration of the Ether Extract

The proposed method involves the extraction and titration of butyric acid in the presence of boric and phosphoric acids. Solutions of these acids were prepared in the approximate concentrations in which they would be present in the reaction mixture at the time it is extracted with ether. Ten milliliters of each solution was extracted as in the method and potentiometric titrations were carried out. The resulting curves are shown in Fig. 1.

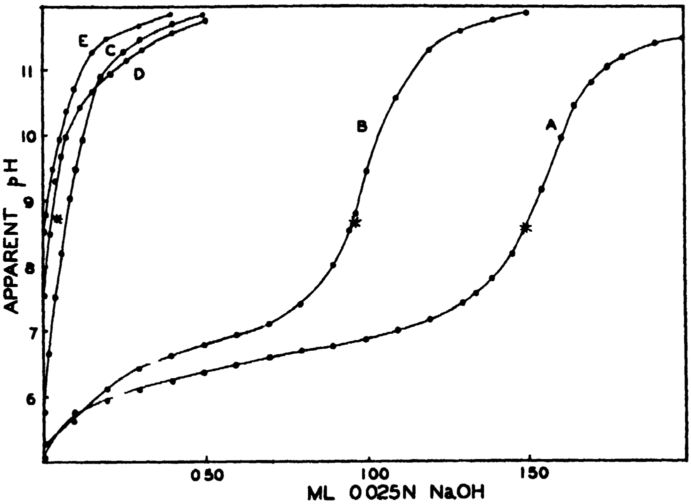

FIG 1 *Potentiometric titration curves of ether extracts of: A, 0 008 M butyric acid, B, 0 005 M butyric acid, C, 0 5 M phosphoric acid, D, 0 05 M boric acid, E, distilled water *Cresol red end point*

It is apparent from these curves that butyric acid is easily extracted and that cresol red provides a suitable end point. The presence of low concentrations of boric and phosphoric acids does not interfere with the titration of the butyric acid.

Extraction of Free Butyric Acid

Increasing amounts of 0.05 *N* butyric acid were added to test tubes containing 7 ml. of buffered pasteurized skim milk after the addition and emulsification of the tributyrin. Following acidification with 3.5 ml of 1.5 *M* phosphoric acid, the determinations were completed as outlined under "Method".

Fig. 2 shows that there was a direct relation between the concentration of free butyric acid in the sample and the amount extracted by the ether. Approximately 90% of the added butyric acid was recovered.

Experiments showed that minor changes in the extraction temperature and procedure, tributyrin concentration, buffer composition, and phosphoric acid concentration had little effect on the extraction of butyric acid.

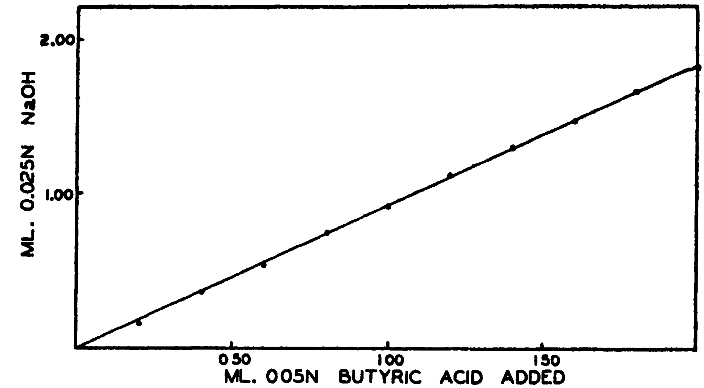

FIG 2 *Extraction of butyric acid.*

SOME FACTORS AFFECTING THE METHOD

Tributyrin Concentration

Experiments were carried out in which the amount of substrate added was varied from 0.00 to 1.20 ml. The determinations were completed in the usual manner except that 3.5 ml. of 1.5 *M* phosphoric acid was used for acidification.

The data obtained for six milks are shown in Fig. 3. Hydrolysis close to the maximum was obtained when 0.60 ml. was used, except in the experiment on the highly active milk *A*. With higher concentrations of tributyrin less

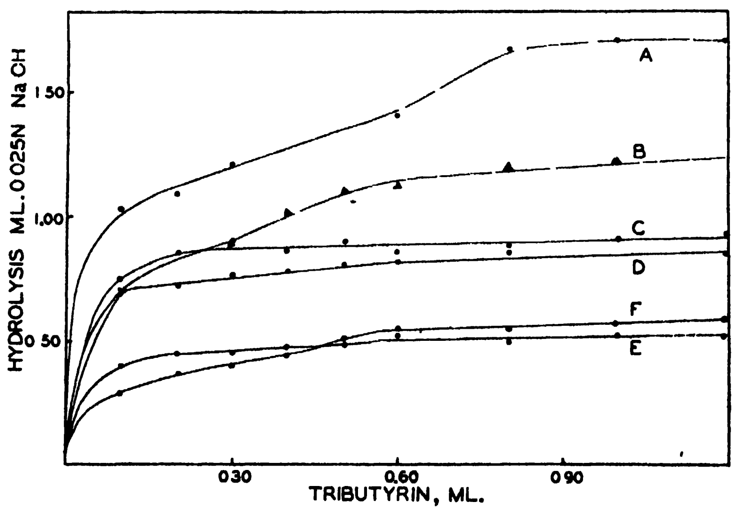

FIG. 3. *Substrate concentration and hydrolysis (six milks).*

ether separates as a clear layer and greater care is necessary in pipetting the 5 ml. aliquot for titration. The great majority of the determinations made on the individual milks of cows in the University of Alberta herd have given hydrolysis values under 1.25 ml. Therefore, 0.6 ml. of tributyrin is used for

Temperature

Fig. 5 shows that in a 30 min. reaction period maximum hydrolysis was at 37° C. and this temperature was chosen for the method.

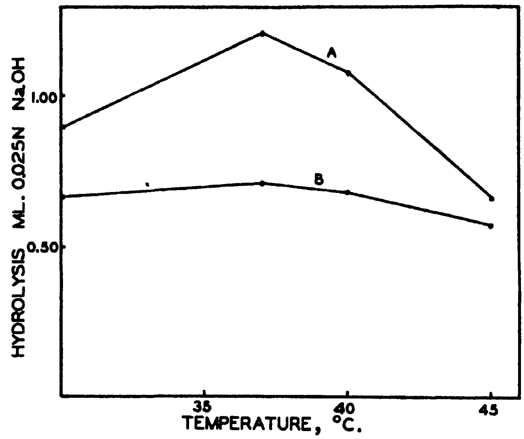

Fig 5 *Reaction temperature and hydrolysis (two milks).*

Length of Reaction Period

Experiments in which the reaction time was varied from 0 to 90 min. showed that for the first 20 min. the rate of hydrolysis was constant and then started to decrease, presumably because of heat-inactivation. Fig. 6

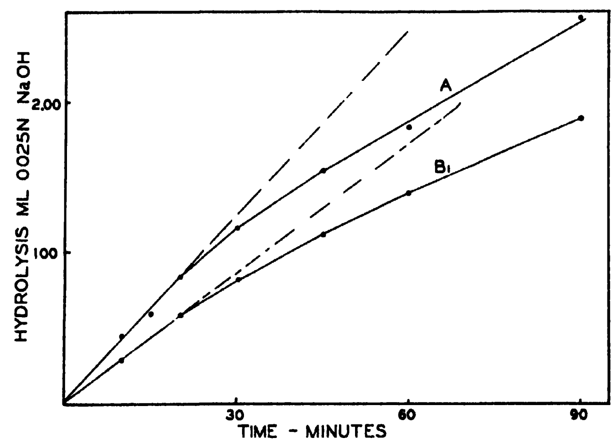

Fig. 6. *Reaction time and hydrolysis (two milks).*

shows the curves obtained in two representative experiments with different milks. Thirty minutes was chosen as the reaction time in order to obtain reasonable hydrolysis and yet avoid marked inactivation of the enzyme.

Enzyme Concentration

Varying amounts of suitable buffers, skim milk, and distilled water were added to test tubes to make a total volume of 7 ml. per tube and, after the

addition of 0.6 ml. of tributyrin, to give pH values of 8.75±0.05. Fig. 7 shows hydrolysis values in two representative trials. It is apparent that in these experiments hydrolysis of the substrate was proportional to the concentration of the enzyme.

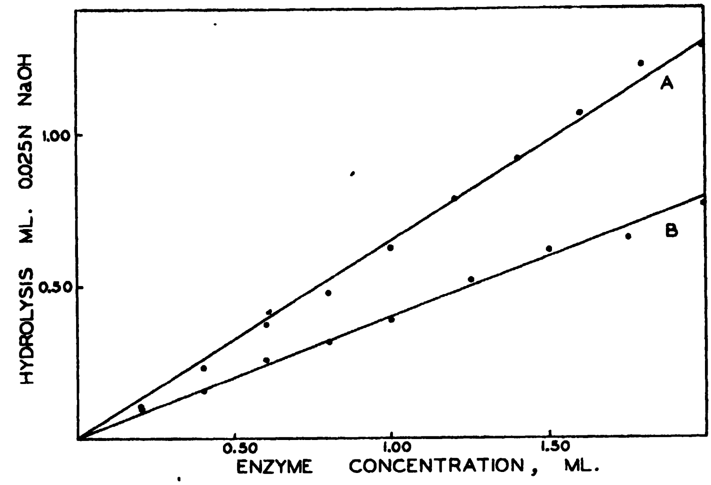

FIG. 7. *Enzyme concentration and hydrolysis (two milks).*

Reproducibility

In general, while duplicate determinations usually check to within ±0.02 ml. and variability among replicates tends to increase with increasing titer, nevertheless, there are some exceptions, as illustrated in Table II.

TABLE II

REPRODUCIBILITY OF LIPASE DETERMINATIONS

Milk	Titer	Blank	Hydrolysis	Total variation
1	1.07 1.07 1.06 1.05	0.22	0.85 0.85 0.84 0.83	0.02
2	1.10 1.10 1.17 1.11	0.23	0.87 0.87 0.94 0.88	0.07
3	1.74 1.80 1.75 1.78	0.21	1.53 1.59 1.54 1.57	0.06
4	2.14 2.18 2.15 2.16	0.24	1.90 1.94 1.91 1.92	0.04

Individual Milks

In the course of this investigation many assays were made on the milks of cows in the University herd, which included Jersey and Holstein breeds. Table III gives representative data for 10 such milks that had been held at 4° C. for approximately two hours after milking. No explanation to account for the variation in the lipase activities of these milks is advanced at this time. Further studies on the possible correlation between various management factors and lipase content of the individual milks are required. Factors such as storage conditions affecting the activity of milk lipase should also be investigated.

TABLE III

LIPASE ESTIMATIONS ON INDIVIDUAL MILKS

Milk	1	2	3	4	5	6	7	8	9	10
Hydrolysis	0.38	0.48	1.16	0.80	1.35	0.51	1.08	0.56	0.56	0.57

Discussion

There is the possibility that milk lipase, which hydrolyzes milk fat, and the enzyme that splits tributyrin may not be identical. Therefore, some authors use the designation tributyrinase for the agent responsible for the latter reaction. The present authors prefer the term lipase until evidence substantiates the double enzyme theory.

The method described permits a comparatively simple and reasonably quantitative estimation of lipase in cow's milk. The lipolytic activity of milk is ordinarily not strong compared to that of some other biological fluids. The short reaction period entailed in this method may be found to be disadvantageous when the lipolytic activity is unusually weak. However, it is believed that the method may serve as a basis for the determination of lipase and the study of lipolysis in dairy products and microbial cultures.

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ESTIMATION OF LIPASE IN DAIRY PRODUCTS

II. AN EXTRACTION-TITRATION METHOD FOR THE ESTIMATION OF BACTERIAL LIPASE[1]

By D. J. Lubert,[2] L. M. Smith,[3] and H. R. Thornton[4]

Abstract

A method of estimating bacterial lipase is presented that is believed to be more nearly quantitative than any other at present available. The method is based on the titration of acids in an ether extract of a skim milk culture following a 30 min period of lipase activity at 37° C. It is shown that ether-soluble acids carried into the reaction medium do not interfere with the measurements and that ether-soluble acids are not produced from protein or lactose during the test The method is applicable over a sufficiently wide pH range to make it generally adaptable in bacteriology.

Introduction

Plating methods of demonstrating bacterially induced lipolysis have limited quantitative value and may be applied only within a restricted pH range. The advantage of their long incubation periods may be lost by the potentialities thus offered for indirect and interfering reactions (4).

The quantitative methods that have been proposed involve alkali titration of an inoculated and incubated emulsion of a fat in a liquid medium (5, 7, 10). These methods have certain disadvantages, including cumbrousness, long incubation periods with possible interfering reactions, titration in the presence of proteins, or obscure end points (8).

The method for estimating milk lipase that was described in the first paper of the present series (9) was suitably modified to measure bacterial lipases. This technique eliminates some of the disadvantages mentioned above and, as will be shown, is flexible over a wide range of conditions.

The Method

Reagents

Borate buffer: 6.23 gm. boric acid and 42 ml. N sodium hydroxide per liter of solution

Titration mixture: 50 ml. 0.1 alcoholic cresol red in 1 liter 95% alcohol and 1 liter distilled water. Adjust mixture to pH 7.4 with 0.05 N sodium hydroxide.

[1] *Manuscript received July 26, 1949*
Contribution from the Department of Dairying, University of Alberta, Edmonton, Alberta. The data contained herein were taken from theses submitted to the University of Alberta by the two senior authors in partial fulfillment of the requirements for the degree of Master of Science. The study was supported by a grant from the Committee on Agricultural Research Grants of the University of Alberta.

[2] *Sessional Instructor in Dairying.*
[3] *Lecturer in Dairying.*
[4] *Professor of Dairying.*

Standard 0.02 *N* sodium hydroxide
Tributyrin
Molar phosphoric acid
Ethyl ether.

Procedure

Ten milliliters of sterile skim milk is inoculated with a loop transfer from an actively growing slant culture of the test organism and incubated for 24 to 48 hr. at the organism's optimum growth temperature.

Two milliliters of this skim milk culture is pipetted into 5 ml. of the borate buffer in a test tube and adjusted, if necessary, to pH 8.5 with normal sodium hydroxide or molar phosphoric acid. This buffered culture is brought to the temperature of a 37° C. water bath within four minutes and 0.2 ml. tributyrin is added and emulsified by vigorous shaking of the stoppered tube for five seconds. The mixture is not further disturbed in the water bath during the remainder of the reaction period.

At the end of the reaction period (30 min. after the addition of the tributyrin) 5 ml. of molar phosphoric acid is added to stop hydrolysis and permit subsequent extraction of the liberated acid. The whole is mixed by inverting twice, brought to the temperature of a 20° C. water bath and shaken vigorously for five seconds with 10 ml. of ethyl ether. Ether layer separation and small water droplet settling are effected in five minutes in the undisturbed tube and then the rubber stopper is loosened. After another three minutes a 5 ml. aliquot of the ether layer is pipetted into a 50 ml. Erlenmeyer or beaker containing 10 ml. of the titration mixture.

Titration is usually with 0.02 *N* sodium hydroxide. It is probable that this concentration will be found generally satisfactory for the assay of bacterial lipase. As titer increases above approximately 1.5 to 2.0, sharper end points are obtained with increasing concentration of sodium hydroxide. By calculation such a titer value is brought to the equivalent 0.02 *N* sodium hydroxide value.

Titer is defined as the average number of milliliters of 0.02 *N* sodium hydroxide required in duplicate titrations. A blank determination is made in a similar manner except that the reaction period is omitted. Lipolysis is expressed as the difference between the sample and blank titers.

Experimental Techniques

In the experimental work the above procedure was followed in almost all cases but occasional variation was desirable. In a few experiments lipolysis was stopped by the addition of 3.5 ml. of 1.5 *M* phosphoric acid in the interests of volume uniformity for extraction.

Buffers other than the standard buffer were 0.1 *M* with respect to boric acid but contained varying amounts of normal sodium hydroxide or molar phosphoric acid.

In the accompanying tables the titer before and the titer after refer to the titers at the start and end of the reaction period.

The main test organism was a strain of *Pseudomonas fluorescens* growing well at 25° C. and poorly at 37° C. *Escherichia coli* was used in two experiments and *Streptococcus lactis* in another.

Plate counts were made according to Standard Methods for the Examination of Dairy Products (2) except that incubation was for three days at 25° C. Unless otherwise stated, the skim milk was reconstituted from Bacto skim milk (dehydrated). Eastman tributyrin was used throughout.

Experimental

Acid Recovery

All acids soluble in ether, if present, contribute to the acidity of the ether extract. Since skim milk is the basic medium, lactic and acetic acids assume particular importance.

Solutions of four ether-soluble acids were standardized as follows: acetic acid, 0.0192 *N*; propionic acid, 0.0192 *N*; butyric acid, 0.0197 *N*; and lactic acid, 0.0152 *N*.

Two milliliters of the acid solution to be tested was added to 7 ml. of buffered fresh skim milk. Acidification was with 3.5 ml. of 1.5 *M* phosphoric acid after the addition of tributyrin. In addition a 2.17 ml. mixture of the four acids in buffered fresh skim milk was assayed. The assay data are shown in Table I.

TABLE I
RECOVERY OF ADDED ACIDS

Acid added	Titer	Blank-corrected titer	% recovery
None	0 16	0 00	—
Acetic	0.39	0 23	23
Propionic	0 73	0 57	57
Butyric	1 06	0 90	90
Lactic	0 25	0 09	12
Mixture	0 62	0 46	46

Butyric acid was the most completely recovered, 90%, and lactic acid the least, 12%. The 46% recovery of the mixture of acids was in close agreement with the theoretical 47% calculated from the percentage recovery of the individual acids. Duplicates checked within 2%. This is confirmatory of the results reported in the first paper of this series, in which 90% recovery of butyric acid was obtained.

Nonfat Sources of Acid

Bacterial cultures may contain ether-soluble acids originating from such sources as protein or carbohydrate. It has been shown above that such acids as acetic, propionic, and lactic are recovered in significant proportions during

ether extraction. This is borne out by the data in Table II, which show that for these species the titers before and after the reaction period are high although there is no lipolysis. It is interesting to note that the titer for *S. lactis* is almost identical with the theoretical, 0.50, if the assumptions are made that only lactic acid was produced in the skim milk by this organism, that the titratable acidity was 0.8% expressed as lactic acid, and that 12% of the lactic acid was recovered in the ether layer.

TABLE II

LIPOLYSIS BY TWO ACID-PRODUCING BACTERIA

Organism	Titer		Lipolysis
	Before	After	
S. lactis	0.48	0.51	0.03
E. coli	0.75	0.77	0.02

These data also show that the ether-soluble acids present in the culture before the reaction period do not interfere with the measurement of the acids produced during that period. They are measured in the blank and are eliminated from consideration by subtraction of the titer of the blank from the sample titer.

This leaves the possibility that protein or lactose is a source of acid produced during the reaction period. Therefore, attempts were made to follow protein and lactose breakdown during the reaction period as set forth in Table III.

TABLE III

PROTEIN AND LACTOSE BREAKDOWN DURING THE REACTION PERIOD

(*P. fluorescens*)

	Titer		Lipolysis	Change in	
	Before	After		Amino N	Lactose
Lipolytic activity	0.25	0.65	0.40	—	—
Amino N (mgm./2 ml. culture)	0.060	0.063	—	+0.003	—
Lactose (gm./2 ml. culture)	0.081	0.080	—	—	−0.001

In this experiment there was a 0.003 mgm. increase of amino nitrogen, as determined by the copper method of Albanese and Irby (1), and this value was very closely duplicated in each of a number of trials. This increase is the equivalent of 0.01 ml. of 0.02 N sodium hydroxide, which is considered to be within the experimental error of the method. It is concluded that ether-soluble acids are not produced from proteins by *P. fluorescens* during the reaction period.

Determinations by the gravimetric method (3) showed the disappearance of 0.001 gm. of lactose during the reaction period. Assuming complete con-

version of this amount of sugar into lactic acid and 12% extraction of the lactic acid by ether, this amount represents only 0.03 ml. of 0.02 *N* sodium hydroxide as used in this test. Although the gravimetric method of measuring small amounts of lactose is of questionable accuracy because it measures not the actual lactose but the reducing capacity of the solution, dissimilation of lactose by this organism is not to be expected. In the light of further evidence it seems probable that lactose decomposition during the reaction period was of no significance whatsoever.

The strain of *P. fluorescens* used as test organism grew so slowly at 37° C. that significant growth was not to be expected during the reaction period at this temperature. This expectation was justified by plate counts, which did not increase during the 30 min. reaction period. However, lactases might well be active at this temperature. Nevertheless, that lactose was not the source of ether-soluble acid produced during the reaction period is shown in Table IV from which it is seen that neither *P. fluorescens* nor *E. coli*, a lactose

TABLE IV
ACID FORMATION DURING THE REACTION PERIOD

Sample	Tributyrin added	Titer		Lipolysis
		Before	After	
Uninoculated skim milk	−	0.17	0.17	0.00
	+	0.20	0.20	0.00
Inoculated with *P. fluorescens*	−	0.17	0.17	0.00
	+	0.20	0.82	0.62
Inoculated with *E. coli*	−	0.69	0.69	0.00
	+	0.71	0.73	0.02

fermenting bacterium, gave evidence of any lipolysis in the absence of tributyrin. It is concluded, therefore, that the possibility of the production of ether-soluble acid from lactose during the reaction period may be ignored.

TABLE V
VARIATIONS IN REPLICATE CULTURES

Culture number	Titer		Lipolysis
	Before	After	
1	0.16	0.83	0.67
2	0.18	0.93	0.75
3	0.18	0.85	0.67
4	0.19	1.03	0.84
5	0.18	0.93	0.75
6	0.18	0.91	0.73
7	0.18	0.90	0.72
8	0.18	0.94	0.76
9	0.18	0.86	0.68
10	0.19	1.08	0.89
Control	0.18	0.19	0.01

Substrate Concentration

The effect of varying the concentration of tributyrin was studied with a 30 hr. and a 48 hr. culture of *P. fluorescens*. Fig. 1 shows that when lipolysis is very strong it is desirable to use a concentration of the substrate greater than 0.2 ml. Nevertheless, it is thought that 0.2 ml. of tributyrin will prove generally satisfactory.

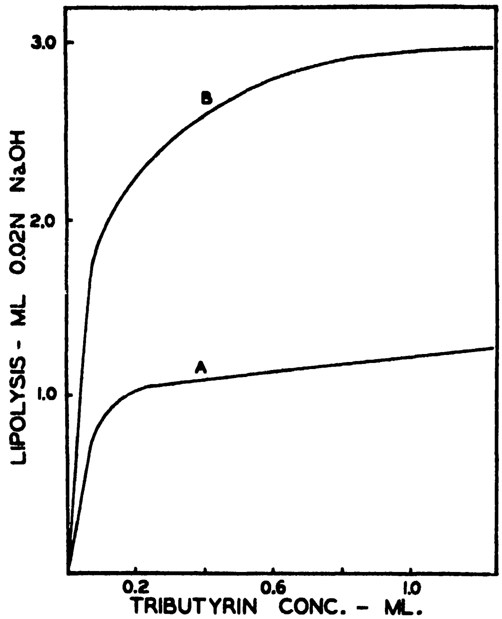

FIG. 1. *Substrate concentration and lipolysis A = 30 hr culture B = 48 hr. culture*

Variations in Replicate Cultures

Replicate tubes, each containing 10 ml. of sterile skim milk, were inoculated by needle from a 24 hr. slant culture of the test organism. These were incubated at 21° C. for 36 hr. and the lipase activity of each was determined. The lipolytic values of 10 such replicates are shown in Table V. The maximum deviation from the mean lipolysis of 0.75 was ±18.6%. This deviation could be expected from probable growth differences in the various replicate cultures.

Amount of Inoculum

The amount of inoculum added to the sterile skim milk before incubation was varied in different ways, using the loop method and pipetting from a water suspension of the test organism. Some variations in lipolysis were noted but these could not be related to the method of inoculation or the amount of inoculum, at least until the latter was large. It is concluded that the loop method is sufficiently accurate for this type of analysis.

pH Range

This method was originally designed to measure milk lipase, which has an optimum activity at approximately pH 8.5. For measuring bacterial lipase

it appeared desirable to know that the method is applicable over a wide pH range.

When the pH during the reaction period was varied, lipolysis by *P. fluorescens* was 2.28 at pH 8.5, 1.37 at pH 7.0, and 1.01 at pH 5.5.

Although it was evident that the method was adaptable over a fairly wide pH range, nevertheless, it seemed desirable to demonstrate its use, not only over a wider pH range, but also with a lipase having an activity optimum on the acid side of neutrality. Therefore, the defatted meat from the dehulled and macerated castor bean (castor bean lipase has an approximate activity optimum at pH 5) was dried, powdered, and suspended in water. Of this suspension 2 ml. was pipetted into 5 ml. of a borate buffer adjusted to the desired pH with normal sodium hydroxide or molar phosphoric acid. A series with varying pH values was so prepared and the pH values determined electrometrically at the start of the reaction period, which in this case was of 60 min. duration. The control titer in each case was determined on a duplicate sample that had been autoclaved for 10 min. at 121° C. before the addition of the buffer. Difficulty was experienced with gel formation in the control samples on shaking with ether. These gels were, however, broken by centrifugalization and offered no further problem. The data from this experiment are presented in Table VI.

TABLE VI
LIPOLYSIS BY CASTOR BEAN LIPASE

pH	Titer		Lipolysis
	Before	After	
2.86	0.24	0.35	0.11
3.10	0.22	0.36	0.14
3.50	0.22	0.73	0.51
3.90	0.22	1.82	1.60
5.95	0.24	1.83	1.59
7.59	0.25	0.32	0.07
8.50	0.24	0.28	0.04
8.72	0.26	0.23	0.00

It is seen that this method measures lipase activity over a sufficiently wide pH range to make it generally applicable in bacteriology.

Discussion

Although extreme accuracy is not claimed for this method, it is believed to offer greater precision than any other method currently available.

It is recognized that, if tributyrin is the only substrate used, tributyrinase may be the only enzyme measured. However, the studies of Collins and Hammer (6) do not point to such narrow specificity of bacterial lipases. In any case the method is adaptable but limited to the study of any substrate that is liquid at room temperature.

The short period during which the enzyme is in contact with the substrate is both an advantage and a disadvantage. It is an advantage in that bacterial growth is eliminated, or nearly so, during this period and extraneous and interfering reactions are held to a minimum. On the other hand, a disadvantage is introduced in that a very slow hydrolysis is not continued long enough to liberate measurable amounts of fatty acid.

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ESTIMATION OF LIPASE IN DAIRY PRODUCTS

III. LIPASE ACTIVITY IN CULTURES OF MICRO-ORGANISMS AND IN CHEESE[1]

By D. J. Lubert,[2] L. M. Smith,[3] and H. R. Thornton[4]

Abstract

The lipolytic activity in skim milk cultures of micro-organisms representing a number of species and genera were studied by the extraction–titration method described in the preceding paper. No evidence was found of a bacterial lipase having an activity optimum on the acid side of neutrality. No lipase active at approximately pH 5.0 was demonstrated in 20 samples of commercial cheddar cheese of varying age or one sample of blue veined cheese on measurement by the extraction–titration method or by the Peterson *et al.* method. Weak lipolytic activity was found in one sample of blue veined cheese by the extraction–titration method. No lipolytic activity at pH 8.5 was demonstrated by the extraction–titration method in the one sample of cheese tested at this pH.

Introduction

The extraction–titration method of measuring bacterial lipase described in the preceding paper of this series (2) was used to compare the lipolytic activity of 10 species of seven bacterial genera, and some unidentified cultures of bacteria, yeasts, and molds. The study also included 22 samples of cheese.

Methods

Incubation of all cultures and plates was for three days at either 25° C. or 37° C. Lipolysis is expressed as in the preceding paper. Observations were made of the action of giant colonies on Nile blue sulphate agar plates containing 0.5% tributyrin (1).

Titration differences of less than 0.05 are arbitrarily interpreted as representing no lipolysis, 0.05 to 0.1 as questionable lipolysis, 0.1 to 1.0 as weak lipolysis, and over 1.0 as strong lipolysis.

The unidentified "apple" bacterium was a chance isolation that produced an apple odor when grown in pure culture in skim milk. The *A* and *B* cultures were pseudomonads producing a peculiar bitter taste in milk or cream held at low temperatures for long periods but growing well at 27° C.

Aqueous extracts for lipase determinations were prepared by either of two methods from commercial cheese selected at random from various sources.

[1] *Manuscript received July 26, 1949.*
Contribution from the Department of Dairying, University of Alberta, Edmonton, Alberta. The data contained herein were taken from theses submitted to the University of Alberta by the two senior authors in partial fulfillment of the requirements for the degree of Master of Science. The study was supported by a grant from the Committee on Agricultural Research Grants of the University of Alberta.
[2] *Sessional Instructor in Dairying.*
[3] *Lecturer in Dairying.*
[4] *Professor of Dairying.*

Some of the extracts were prepared by the method of Peterson *et al.* (3) and assayed by the extraction–titration method. The following procedure was used for obtaining the remaining extracts.

Twenty-five grams of the cheese sample was ground in a mortar with sand, and transferred to a 125 ml. Erlenmeyer. This was shaken successively with 50 ml., 25 ml., and 25 ml. of water for 10, 5, and 5 min. respectively. The washings with the suspended material were combined in a 250 ml. centrifuge bottle and centrifuged for 10 min. at 2000 r.p.m. Two-milliliter aliquots were buffered at approximately pH 5.0 and used for the extraction–titration assay. A 10 ml. aliquot of the cheese extract was removed and diluted with water to 25 ml., and 5 ml. of this diluted aliquot was used for lipase determination by the Peterson *et al.* method.

The reaction period in the cheese lipase determinations was of 30 to 60 min. duration while the buffer used was a mixture of phosphoric acid, disodium phosphate, and sodium hydroxide in the proportion necessary to buffer the extract at approximately pH 5.0.

Experimental

Lipolysis by Various Micro-organisms

Scrutiny of Table I reveals that by the criterion of this method nonlipolytic bacteria include *Streptococcus lactis*, *Aerobacter aerogenes*, *Escherichia coli*,

TABLE I

LIPOLYTIC ACTIVITY OF VARIOUS MICRO-ORGANISMS

Arbitrary classification	Organism	Titer		Lipolysis	N.b.s. agar
		Before	After		
No lipolysis	Control	0.18	0.17	0.00	
	S. lactis,	0.48	0.51	0.03	–
	A. aerogenes	0.31	0.32	0.01	–
	E. coli	0.75	0.77	0.02	–
	B. subtilis	0.25	0.22	0.00	–
	P. putrefaciens	0.25	0.23	0.00	+
	S. albus	0.24	0.28	0.04	+
	"Apple" bacterium	0.15	0.16	0.01	+
	Yeast	0.19	0.20	0.01	
Questionable lipolysis	*A. faecalis*	0.17	0.23	0.06	+++
	S. aureus	0.23	0.30	0.07	+++
	Mold	0.17	0.23	0.06	
	B 1	0.17	0.23	0.06	
	B 2	0.15	0.22	0.07	
Weak lipolysis	*M. smegmatis*	0.15	0.27	0.12	+++
	A 1	0.16	0.28	0.12	
	A 2	0.17	0.27	0.10	
	A 3	0.16	0.33	0.17	
	B 3	0.16	0.54	0.38	
Strong lipolysis	*P. fluorescens*	0.26	3.90	3.64	++++

Bacillus subtilis, *Pseudomonas putrefaciens*, *Staphylococcus albus*, the "apple odor" and yeast cultures. *Alcaligenes faecalis*, *Staphylococcus aureus*, two of the *B* cultures, and the mold were questionably lipolytic. *Mycobacterium smegmatis* and the *A* and B_8 cultures were weakly lipolytic, while *Pseudomonas fluorescens* exhibited strong lipolysis.

This method and the Nile blue sulphate (N.b.s.) agar method were in general but not complete agreement. Moreover, this method did not demonstrate lipolysis by some organisms well known to be lipolytic, such as *Staphylococcus* (5). The probable explanation is to be found in the short time of contact (30 min.) between the enzyme and the substrate. It should also be noted that in this method lipolysis is effected at pH 8.5, while the Nile blue sulphate agar is at approximately pH 7.0. Enzyme activity may vary markedly within this pH range.

It is evident that this method is not adequate for measuring small differences arising from slow enzyme action or bacterial elaboration of small amounts of enzyme. On the other hand, long reaction periods may, and probably frequently do, lead to interfering extraneous reactions such as ether-soluble acid production.

It is interesting to note that the blank titers of the lactose fermenters, *S. lactis*, *A. aerogenes*, and *E. coli* were high. The probable explanation is that ether-soluble acids, mainly lactic and acetic, were carried over from the skim milk cultures. They are, however, eliminated from the lipolysis figures, which are blank-corrected values. It is to be noted that the blank titer of *A. aerogenes* is lower than that of *E. coli* but no explanation is attempted nor was the relation between the bitter flavor and lipolysis by the *A* and *B* organisms studied.

Relation to pH

In estimating the lipolytic activity of micro-organisms recognition must be given to the possibility that different lipases have differing pH optima. The data in Table II do not indicate such a probability, at least for the six organisms tested. *P. fluorescens* exhibited decreasing lipolysis with decreasing

TABLE II

LIPOLYTIC ACTIVITY OF SOME MICRO-ORGANISMS AT VARIOUS ACIDITIES

Organism	Lipolysis		
	pH 5 5	pH 7 0	pH 8 5
Skim milk	0 00	0 00	0 02
P fluorescens	1 01	1 37	2 28
S albus	0 00	0 03	0 05
E. coli	0 00	0 05	0 04
B subtilis	0 00	0,03	0 07
A faecalis	0 03	0 06	0 07
Mold	0 00	0 00	0 03

pH, while none of the other species was lipolytic at any pH. It is interesting that *P. fluorescens*, which produces a lipase with optimum activity above pH 8.0, showed considerable lipolytic activity at pH 5.

Cheddar cheese not infrequently becomes rancid and any enzyme causing this defect must be active at the pH of the cheese, which is usually approximately 5.0. In this connection there has not been complete unanimity of opinion as to the role of milk lipase, which is most active on the alkaline side of neutrality (4). Peterson *et al.* (4) regard lipolytic activity in cheese as being bacterially induced and have reviewed the pertinent literature.

Because of the pH of cheddar cheese and because the extraction–titration method is adaptable to measurement of lipase activity at such a low pH, the method was applied to a number of cheese samples. When no lipolysis was demonstrated in eight cheddar and one blue veined cheese, further samples were assayed by the Peterson *et al.* method as well.

It is to be noted (Table III) that, with one exception, there is no suggestion of significant lipase activity by either method of assay. One blue veined cheese exhibited measurable lipolysis as determined by the extraction–titration method.

TABLE III

LIPASE IN CHEESE

Cheese		Reaction time, min	Extraction–titration method			Peterson et al.
			Titer		Lipolysis	
Sample No.	Age, days		Before	After		Lipase units/ml.
1	15	45	0 21	0.24	0.03	
2	27	45	0.19	0.23	0 04	
3	54	45	0.20	0 24	0.04	
4	91	45	0.25	0.25	0.00	
5	Unknown	30	0.22	0.23	0.01	
6	150	30	0.19	0 19	0.00	
7	150	30	0 20	0.20	0.00	
8	Unknown	60	0.34	0 36	0.02	
9	Unknown	60	0.31	0 32	0.01	
10	Unknown	60	0.41	0.55	0.14	0.01
11	19	60	0.32	0.32	0.00	0.00
12	23	60	0.33	0.33	0.00	0.01
13	27	60	0.33	0 33	0.00	0.00
14	30	60	0.27	0.28	0.01	0.00
15	30	60	0.33	0.33	0.00	0.00
16	35	60	0.27	0.28	0.01	0.00
17	37	60	0.26	0.28	0.02	0.00
18	37	60	0.28	0.27	0.00	0.00
19	40	60	0.29	0.33	0.04	0.00
20	47	60	0.26	0.28	0.02	0.01
21	48	60	0.28	0.28	0.00	0.01
22	54	60	Spoiled	Spoiled	—	0.00

NOTE: *Samples 8 and 10 are blue veined cheese. All others are cheddar cheese.*

There is the possibility of the presence of a lipase active at pH 8.5 but insufficiently active at pH 5 to cause measurable hydrolysis of the tributyrin within 60 min. Cheese number 9, sold as "old Ontario" cheese, was assayed by the extraction–titration method at nine pH values varying from pH 4.67 to pH 9.54. No lipase activity was demonstrated.

Discussion

It would appear that bacterial lipase most vigorously active on the acid side of neutrality is not a common concomitant of bacterial growth. This receives confirmation in the low incidence of rancid cheese.

The theory of a cheese lipase characterized by acid stimulation, whether of bacterial or milk origin, is difficult to reconcile, not only with these studies, but also with common observation of cheese rancidity. The dilatory way in which cheddar cheese acquires this defect lends support to the view that bacterial lipase capable of hydrolyzing the fat in cheese has very weak activity at pH 5. There is no apparent explanation for the variance of these results with those of Peterson *et al* (3)

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ESTIMATION OF LIPASE IN DAIRY PRODUCTS

IV. LIPOLYTIC ACTIVITY OF *PSEUDOMONAS FLUORESCENS*[1]

By D. J. Lubert[2], L. M. Smith[3], and H. R. Thornton[4]

Abstract

The lipolytic activity of a strain of *Pseudomonas fluorescens* was investigated. Under the investigational conditions activity was greatest when the reaction medium was at approximately pH 8.9 at the start of the reaction period and when the reaction was carried out at approximately 42° C. The optimum pH for activity by this enzyme was found to be between 8 and 9. This lipase is not specific for tributyrin but hydrolyzes tricaproin and tricaprylin as well, although with decreasing ease. Calcium chloride inhibited rather than enhanced the activity. Lipolytic activity was greater in nutrient broth-base media than in skim milk but the latter was more satisfactory with which to work. Lipolytic activity and fluorescence were not found to be related. Nutrient broth freed of carbohydrate by *Escherichia coli* growth and heat-sterilized stimulated production of fluorescence.

Introduction

Pseudomonas fluorescens had greater lipolytic activity than any of the other bacteria used in these studies. This species is widespread in the waters of the province, occurs almost universally in such products as raw milk and cream, and is frequently concerned with the production of rancidity in these products. A study of the characteristics of the lipase elaborated by this organism was, therefore, considered to be worthwhile.

Methods

Unless otherwise stated, lipolytic activity was measured by the extraction–titration method as described in the second paper of this series (3). The strain of *P. fluorescens* was the same as was used as test organism in the previous studies. It grew well at 21° to 27° C but very poorly at 37° C. Except as noted, incubation was at 25° C.

Experimental

pH

Lipolysis in a 48 hr. culture (Fig. 1) and a 24 hr. culture (Fig. 2) was determined over a wide range of pH values of the buffered culture at the start of the reaction period. Maximum lipolysis is seen to have been at pH 8.87 in

[1] *Manuscript received July 26, 1949.*
Contribution from the Department of Dairying, University of Alberta, Edmonton, Alberta. The data contained herein were taken from theses submitted to the University of Alberta by the two senior authors in partial fulfillment of the requirements for the degree of Master of Science. The study was supported by a grant from the Committee on Agricultural Research Grants of the University of Alberta.
[2] *Sessional Instructor in Dairying.*
[3] *Lecturer in Dairying.*
[4] *Professor of Dairying.*

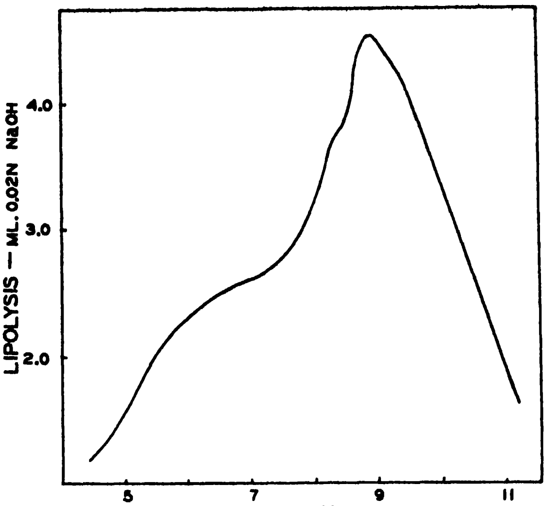

FIG. 1 *pH and lipolysis (48 hr culture)*

Fig. 1 and 8.92 in Fig 2. The 24 hr culture showed very high lipolysis at pH 11 (not shown in Fig 1) This was believed to be caused by saponification of the tributyrin, which was subsequently found not to be a source of inaccuracy in this method at pH 9 or below Similar saponification was

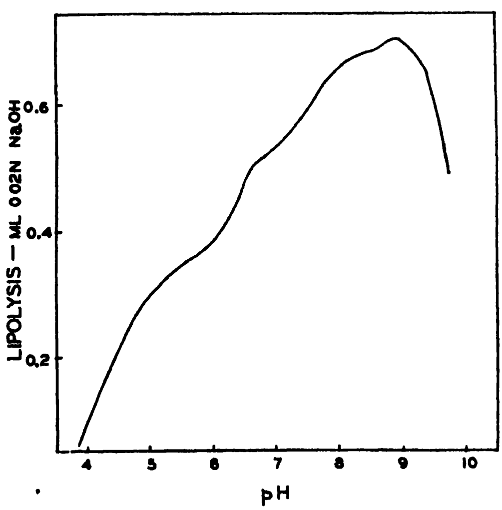

FIG 2 *pH and lipolysis (24 hr. culture).*

not observed in the 48 hr. culture at pH 11, probably because the pH was rapidly lowered during the reaction period.

It cannot be concluded from these data that pH 8.9 is the optimum for activity by this enzyme, because of possible pH changes in the medium during

the reaction period. This is illustrated in Table I, which gives the pH values of the medium at intervals during the reaction period. Trial 1 represents a culture exhibiting low lipolysis while a higher concentration of the enzyme was present in Trial 2. In each case the pH of the medium decreased as

TABLE I

pH CHANGES DURING THE REACTION PERIOD

Trial	Lipolysis	Reaction time, min							Total decrease pH units
		0	5	10	15	20	25	30	
1	0.34	8.41	8.37	8.51	8.34	8.36	8.31	8.32	0.09
	0.37	8.54	8.52	8.59	8.49	8.51	8.48	8.48	0.06
	0.35	8.84	8.83	8.83	8.81	8.80	8.78	8.76	0.08
2	2.77	8.42				7.89		7.55	0.87
	2.90	8.68		8.49		8.26		8.00	0.68
	2.82	8.91		8.75		8.55		8.37	0.54

lipolysis progressed. That the changes were related to the liberation of free butyric acid is substantiated by the fact that the addition of 1.2 ml. of 0.92 *N* butyric acid to the usual quantity of buffered medium lowered the pH from 8.81 to 8.3. This concentration of butyric acid is the equivalent of a lipolysis value of 2.9, which is in very close agreement with the results of Trial 2.

The conclusion appears to be justified that this enzyme exhibits maximum activity at pH values between 8 and 9.

Temperature

Lipolysis was determined in the usual manner with an 18 hr. skim milk culture grown at 25° C. The reaction temperature of replicate tubes was varied, using water baths adjusted to 6°, 19°, 26°, 37.5°, 41.5°, 46.5°, and 52° C. The results are graphed in Fig 3 (Curve A).

This experiment was repeated but a 24 hr. skim milk culture was held at 4.5° C. for seven days before the test. The reaction temperatures were 37°, 42°, 47°, and 51° C. (Fig. 3, Curve B).

It will be observed that the optimum temperature for activity of this lipase is approximately 42° C.

Heat has a double effect on the activity of the enzyme. It stimulates activity by supplying energy and it retards activity by denaturing the enzyme. Below the optimum temperature the first influence dominates and lipolysis increases. Above the optimum temperature the second influence becomes major and lipolysis decreases The curves suggest that this lipase would be completely inactivated during milk pasteurization (62° C. for 30 min.).

Substrate Specificity

In a study of substrate specificity tricaproin and tricaprylin were substituted for tributyrin. Table II shows that all three triglycerides were attacked

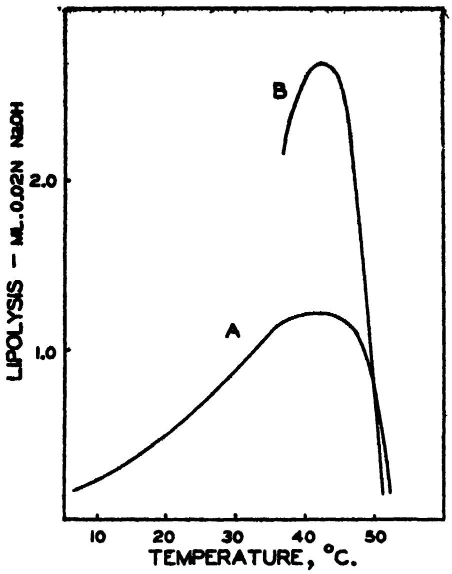

FIG 3 *Temperature and lipolysis.*

although ease of hydrolysis decreased with increasing molecular weight. This confirms the observations of Collins and Hammer (1) that bacterial lipase is not characterized by narrow substrate specificity.

TABLE II

LIPOLYSIS OF THREE TRIGLYCERIDES

Substrate	Titer		Lipolysis
	Before	After	
Tributyrin	0 23	2 09	1 86
Tricaproin	0 70	1 22	0 52
Tricaprylin	0 34	0 64	0 30

Calcium Chloride

Smith (4) found that 0.25 ml. of 10% calcium chloride per 2 ml. of milk increased the activity of milk lipase. The same concentration of calcium chloride in the reaction mixture tended to retard the activity of *P. fluorescens* (Table III).

TABLE III

INHIBITION BY CALCIUM CHLORIDE

Calcium chloride	Titer		Lipolysis
	Before	After	
Not added	0 32	3.34	3 02
Added	0 32	2 79	2.47

Media

In preliminary experiments 0.7% peptone solution was observed to be unsatisfactory for promoting elaboration of lipase by this organism. Jamieson's (2) modification of Sullivan's "*K*" medium was little better, while skim milk reconstituted from powder Soxhlet-extracted with ether for 24 hr. was the equivalent of the nonextracted skim milk.

The results of a study with modified nutrient broth are given in Table IV. The carbohydrate-free broth was prepared by growing *Escherichia coli* in

TABLE IV

LIPOLYSIS IN VARIOUS MEDIA

Medium	Titer		Lipolysis
	Before	After	
Broth	0.22	0.53	0.31
Broth + 0.05% sodium caseinate	0.17	0.59	0.42
Broth + 0.05% agar	0.17	0.45	0.28
Broth, carbohydrate free	0.19	0.46	0.27
Broth + 0.15% butter oil	0.17	0.34	0.17
Skim milk	0.20	0.35	0.15
Broth, uninoculated	0.13	0.15	0.02
Skim milk, uninoculated	0.18	0.18	0.00

nutrient broth for 24 hr. at 37° C., after which the culture was filtered through a Berkefeld filter and the filtrate was autoclaved.

Greater lipolysis was obtained with the broth-base media than with the skim milk. This is confirmed by the data in Table V, in which nutrient broth is shown to be superior to skim milk for the encouragement of lipolysis by young cultures but slightly inferior for old cultures. The reason for this is obscure but may be related to growth rates of *P. fluorescens* in different media.

TABLE V

LIPOLYSIS IN THREE MEDIA

Medium	Lipolysis after incubation for		
	24 hr.	48 hr.	96 hr.
Skim milk	0.29	0.86	2.63
Nutrient broth	0.57	1.25	2.13
Carbohydrate-free broth	0.47	1.69	3.10

There is, however, a serious objection to the use of broth-base media in this technique, very considerable difficulty was encountered with gel formation on the addition of ether. Skim milk cultures were found to give more reliable results with more uniform reproducibility. The presence of fat in the medium seems to be unnecessary for lipase elaboration by this organism.

Fluorescence

It was observed that cultures of *P. fluorescens* in the carbohydrate-free broth took on a marked green coloration. The possible relation between lipolysis and fluorescence was, therefore, studied. Unless labeled uninoculated (Table VI), the various media were inoculated with *P. fluorescens,* incubated at 21° C. for three days and given dark-room examination in ultraviolet light.

TABLE VI

FLUORESCENCE PRODUCTION IN VARIOUS MEDIA

Culture medium	Fluorescence	
	Amount	Color
"*K*" medium	++++	Bright green
Nutrient broth	+	Faint green
Nutrient broth inoculated with both *P. fluorescens* and *E. coli*	+	Faint green
Nutrient broth filtrate (Berkefeld filter), autoclaved	+	Faint green
Nutrient broth filtrate (Berkefeld filter), not autoclaved	+	Faint green
Nutrient broth culture of *E. coli*, autoclaved	+	Faint green
Carbohydrate-free broth	+++	Bright green
"*K*" medium, uninoculated	0	None
Nutrient broth, uninoculated	+	Light blue

Since cultures in "*K*" medium are highly fluorescent and poorly lipolytic, broth cultures poorly fluorescent and highly lipolytic, and carbohydrate-free broth cultures highly lipolytic and highly fluorescent, it is concluded that lipolysis and fluorescence are not related.

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SECTION F

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SECTION F

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Subjects

ERRATA

VOLUME 26, 1948

KLEINLOGEL'S RAHMENFORMELN PAPER

Page	Line	In place of	Write
555	Last	$-\frac{h}{6}\cdot 3/2 = -\frac{h}{4}$	$+\frac{h}{6}\cdot 9/4 = +\,3/8\, h$
556	2nd	$-\left(\frac{h}{4I_2} + 0 + \frac{h}{4I_2}\right) = -\frac{h}{2I_2}$	$+\left(3/8\,\frac{h}{I_1} + 0 - \frac{h}{8I_1}\right) = +\frac{h}{4I_1}$
	5th	$7/8\,\frac{h}{I_2} + \frac{1}{12}\frac{I}{I_1}$	$7/8\,\frac{h}{I_1} + \frac{1}{12}\frac{1}{I_2}$
		$\frac{l}{I_2}$	$\frac{h}{2I_1} + \frac{1}{I_2}$
		$7/8\,\frac{h}{I_2} + \frac{1}{12}\frac{l}{I_1}$	$7/8\,\frac{h}{I_1} + \frac{1}{12}\frac{l}{I_2}$
	6th	$-\frac{h}{2I_2}$	$+\frac{h}{4I_1}$
		$-\frac{h}{2I_2}$	$+\frac{h}{4I_1}$
		$-\left(1/8\,\frac{h}{I_2} + \frac{1}{12}\frac{l}{I_1}\right)$	$-\left(1/8\,\frac{h}{I_1} + \frac{1}{12}\frac{l}{I_2}\right)$
	9th	$\frac{I_1}{I_2}\cdot\frac{h}{l}$	$\frac{I_2}{I_1}\cdot\frac{h}{l}$
	14th	$-\frac{Ph}{12}\cdot\frac{h}{I_2} - \frac{Ph}{12}\frac{l}{I_1}$	$-\frac{Ph}{12}\frac{h}{I_1} - \frac{Ph}{18}\cdot\frac{l}{I_2}$
	15th	$\frac{Ph}{6}\frac{h}{I_2}$	0
	16th	$\frac{Ph}{12}\frac{h}{I_2} + \frac{Ph}{12}\frac{l}{I_1}$	$+\frac{Ph}{12}\frac{h}{I_1} + \frac{Ph}{18}\frac{l}{I_2}$
	18th	$-\frac{k}{2}$	$+\frac{k}{4}$
		$-\frac{Ph}{12}(k+1)$	$-\frac{Ph}{12}\left(k + \frac{2}{3}\right)$
	19th	$-\frac{k}{2}$	$+\frac{k}{4}$

ERRATA—Continued

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Page	Line	In place of	Write
556	19th	1	$\frac{1}{2} k + 1$
		$- k/2$	$+ k/4$
		$\frac{Ph}{6} k$	0
	20th	$- \frac{k}{2}$	$+ \frac{k}{4}$
		$+ \frac{Ph}{12}(k + 1)$	$+ \frac{Ph}{12}(k + 2/3)$